Environmentalica Fennica 24

Characterisation and source identification of pollution episodes caused by long-range transported aerosols

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Academic dissertation in Environmental Sciences

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To be presented, with the Permission of the Faculty of Biosciences of the University of Helsinki, for public criticism in Auditorium XV of the University Main Building, Unioninkatu 34, on October 12, 2007, at 12 o'clock noon.

Helsinki 2007

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Environmentalica Fennica 24
ISSN 1236-3820

ISBN 978-952-10-4174-7 (paperback)
ISBN 978-952-10-4175-4 (PDF), available from http://ethesis.helsinki.fi

Helsinki University Printing House
Helsinki 2007

Abstract: Characterisation and source identification of pollution episodes caused by long-range transported aerosols. Jarkko Niemi 2007. Faculty of Biosciences, University of Helsinki.

Aerosol particles can cause detrimental environmental and health effects. The particles and their precursor gases are emitted from various anthropogenic and natural sources. It is important to know the origin and properties of aerosols to efficiently reduce their harmful effects. The diameter of aerosol particles (D_p) varies between ~0.001 and ~100 μm. Fine particles ($PM_{2.5}$: D_p < 2.5 μm) are especially interesting because they are the most harmful and can be transported over long distances.

The aim of this thesis is to study the impact on air quality by pollution episodes of long-range transported aerosols affecting the composition of the boundary-layer atmosphere in remote and relatively unpolluted regions of the world. The sources and physicochemical properties of aerosols were investigated in detail, based on various measurements (1) in southern Finland during selected long-range transport (LRT) pollution episodes and unpolluted periods and (2) over the Atlantic Ocean between Europe and Antarctica during a voyage. Furthermore, the frequency of LRT pollution episodes of fine particles in southern Finland was investigated over a period of 8 years, using long-term air quality monitoring data.

In southern Finland, the annual mean $PM_{2.5}$ mass concentrations were low but LRT caused high peaks of daily mean concentrations every year. At an urban background site in Helsinki, the updated WHO guideline value (24-h $PM_{2.5}$ mean 25 μg m^{-3}) was exceeded during 1-7 LRT episodes each year during 1999-2006. The daily mean concentrations varied between 25 and 49 μg m^{-3} during the episodes, which was 3-6 times higher than the mean concentration in the long term.

The in-depth studies of selected LRT episodes in southern Finland revealed that biomass burning in agricultural fields and wildfires, occurring mainly in Eastern Europe, deteriorated air quality on a continental scale. The strongest LRT episodes of fine particles resulted from open biomass-burning fires but the emissions from other anthropogenic sources in Eastern Europe also caused significant LRT episodes. Particle mass and number concentrations increased strongly in the accumulation mode (D_p ~ 0.09-1 μm) during the LRT episodes. However, the concentrations of smaller particles (D_p < 0.09 μm) remained low or even decreased due to the uptake of vapours and molecular clusters by LRT particles.

The chemical analysis of individual particles showed that the proportions of several anthropogenic particle types increased (e.g. tar balls, metal oxides/hydroxides, spherical silicate fly ash particles and various calcium-rich particles) in southern Finland during an LRT episode, when aerosols originated from the polluted regions of Eastern Europe and some open biomass-burning smoke was also brought in by LRT. During unpolluted periods when air masses arrived from the north, the proportions of marine aerosols increased. In unpolluted rural regions of southern Finland, both accumulation mode particles and small-sized (D_p ~ 1-3 μm) coarse mode particles originated mostly from LRT. However, the composition of particles was totally different in these size fractions. In both size fractions, strong internal mixing of chemical components was typical for LRT particles. Thus, the aging of particles has significant impacts on their chemical, hygroscopic and optical properties, which can largely alter the environmental and health effects of LRT aerosols.

Over the Atlantic Ocean, the individual particle composition of small-sized (D_p ~ 1-3 μm) coarse mode particles was affected by continental aerosol plumes to distances of at least 100-1000 km from the coast (e.g. pollutants from industrialized Europe, desert dust from the Sahara and biomass-burning aerosols near the Gulf of Guinea). The rate of chloride depletion from sea-salt particles was high near the coasts of Europe and Africa when air masses arrived from polluted continental regions. Thus, the LRT of continental aerosols had significant impacts on the composition of the marine boundary-layer atmosphere and seawater.

In conclusion, integration of the results obtained using different measurement techniques captured the large spatial and temporal variability of aerosols as observed at terrestrial and marine sites, and assisted in establishing the causal link between land-bound emissions, LRT and air quality.

Keywords: Aerosol particles, long-range transport, pollution episodes, source identification, open biomass burning, chemical composition, individual particle analysis, electron microscopy, mixing state, number size distribution

ACKNOWLEDGEMENTS

This work was carried out at the Department of Biological and Environmental Sciences, University of Helsinki. I am grateful to my colleagues at the Department for the opportunity to undertake this work in an inspiring and interdisciplinary atmosphere. I express my warm thanks to Prof. Pekka Kauppi for important contacts, comments and support during these PhD studies.

I express my deepest gratitude to my excellent supervisor Docent Heikki Tervahattu (Nordic Envicon Oy), who offered me the opportunity to work in stimulating and challenging research projects. I thank him for his patience in guiding me, for letting me try my own ideas and for giving me sharp and encouraging feedback. I also thank my other coauthors for fruitful cooperation, which was crucial for the work: Risto Hillamo, Aki Virkkula, Sanna Saarikoski, Timo Mäkelä, Markus Sillanpää, Kimmo Teinilä, Minna Rantamäki, Ulla Makkonen and Minna Aurela (Finnish Meteorological Institute), Markku Kulmala, Hanna Vehkamäki, Jyrki Martikainen, Lauri Laakso, Larisa Sogacheva, Tareq Hussein and Ismo K. Koponen (Department of Physical Sciences, University of Helsinki), Tarja Koskentalo and Päivi Aarnio (Helsinki Metropolitan Area Council) and Tea Luoto (Department of Biological and Environmental Sciences, University of Helsinki).

Prof. Mihály Pósfai (University of Pannonia) and Dr. Matti Johansson (United Nations Economic Commission for Europe) reviewed this thesis and their commets improved it substantially.

I thank my colleagues at the following institutes for their collaboration: Pasi Aalto and Veijo Hiltunen (Department of Physical Sciences, University of Helsinki), Jaakko Kukkonen, Jussi Paatero and Timo Salmi (Finnish Meteorological Institute), Kaarle Kupiainen (Nordic Envicon Oy and Finnish Environment Institute), Mika Räisänen (Geological Survey of Finland), Jyrki Juhanoja (Top Analytica Oy), Kari Lounatmaa (Helsinki University of Technology), Eija Jokitalo and Mervi Lindman (Electron Microscopy Unit, Institute of Biotechnology), Anu Kousa and Maria Myllynen (Helsinki Metropolitan Area Council), and Esa Tulisalo, Arun Mukherjee, Martin Lodenius and Hannele Pulkkinen (Department of Biological and Environmental Sciences, University of Helsinki).

I acknowledge the following organizations for funding of the research: the Helsinki University Environmental Research Centre (HERC), the Finnish Cultural Foundation (SKR), the Academy of Finland and the Helsinki Metropolitan Area Council (YTV).

My warmest thanks belong to my family and friends. I am grateful to my parents, Leena and Jussi, for their love and support throughout my life. I especially want to thank my beloved wife Minttu and sons Aarni and Touko.

Helsinki, September 2007

Jarkko Niemi

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis consists of an introductory review part, followed by four original research articles. The papers are reproduced with the kind permission of the journals concerned. The references to the articles are indicated in the text by their Roman numerals. In addition, some previously unpublished data and results are presented (indicated in the text with **UP** and described at the beginning of section 3).

I Niemi, J.V., Tervahattu, H., Vehkamäki, H., Kulmala, M., Koskentalo, T., Sillanpää, M. & Rantamäki, M. 2004: Characterization and source identification of a fine particle episode in Finland. Atmospheric Environment 38(30): 5003-5012.

II Niemi, J.V., Tervahattu, H., Vehkamäki, H., Martikainen, J., Laakso, L., Kulmala, M., Aarnio, P., Koskentalo, T., Sillanpää, M. & Makkonen, U. 2005: Characterization of aerosol particle episodes in Finland caused by wildfires in Eastern Europe. Atmospheric Chemistry and Physics 5: 2299-2310.

III Niemi, J.V., Saarikoski, S., Tervahattu, H., Mäkelä, T., Hillamo, R., Vehkamäki, H., Sogacheva, L. & Kulmala, M. 2006: Changes in background aerosol composition in Finland during polluted and clean periods studied by TEM/EDX individual particle analysis. Atmospheric Chemistry and Physics 6: 5049-5066.

IV Niemi, J.V., Tervahattu, H., Virkkula, A., Hillamo, R., Teinilä, K., Koponen, I.K. & Kulmala, M. 2005: Continental impact on marine boundary layer coarse particles over the Atlantic Ocean between Europe and Antarctica. Atmospheric Research 75(4): 301-321.

AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

I Niemi planned the research in cooperation with the coauthors and performed the SEM/EDX and data analysis. He planned and wrote the manuscript, except the particle mass and number size distribution section. Final editing of the paper was made together with the other authors.

II Niemi planned the research with the coauthors and performed the SEM/EDX and data analysis. He outlined and wrote the manuscript, except the particle mass and number size distribution section, which was written in cooperation with the other authors. The final version of the paper was modified, based on comments from the coauthors.

III Niemi planned the research with the other authors and performed the TEM/EDX and data analysis. He was responsible for writing and processing the paper. Some changes were made, based on comments from the other authors.

IV Niemi planned the research with the other authors and performed the SEM/EDX and data analysis. He was responsible for writing the first version of the manuscript, which was then edited in cooperation with the coauthors.

ABBREVIATIONS

BC	Black carbon
CCN	Cloud condensation nucleus
CNC	Condensation nucleus counter
D_{50}	50% aerodynamic cutoff diameter
D_p	Particle diameter
DMA	Differential mobility analyser
DMPS	Differential mobility particle sizer
DMS	Dimethyl sulphide
DRH	Deliquescence relative humidity
EC	Elemental carbon
ERH	Efflorescence relative humidity
ELPI	Electrical low pressure impactor
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
FAO	Food and Agricultural Organization
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory model
IC	Ion chromatograph
IPCC	Intergovernmental Panel of Climate Change
LC/MS	Liquid chromatograph coupled with mass spectrometer
LRT	Long-range transport
MBL	Marine boundary layer
MODIS	MODerate-resolution Imaging Spectroradiometer
MSA	Methanesulphonate
NAAPS	Navy Aerosol Analysis and Prediction System
NOAA	National Oceanographic and Atmospheric Administration
NO_x	Nitrogen oxides ($NO_x = NO + NO_2$)
Nss-SO_4^{2-}	Non-sea-salt sulphate
OC	Organic carbon
OM	Organic matter
PAH	Polycyclic aromatic hydrocarbon
PM_x	Particulate matter with an aerodynamic diameter smaller than x μm
PM_{x-y}	Particulate matter with an aerodynamic diameter between x and y μm
$PM_{>x}$	Particulate matter with an aerodynamic diameter larger than x μm
POA	Primary organic aerosol
RH	Relative humidity
SD	Standard deviation
SEM/EDX	Scanning electron microscope coupled with energy-dispersive X-ray microanalyser
∑MA	Sum of monosaccharide anhydrides (levoglucosan + galactosan + mannosan)
SOA	Secondary organic aerosol
SSP	Sea-salt particle
SVOC	Semivolatile organic compound
TC	Total carbon
TEM/EDX	Transmission electron microscope coupled with energy-dispersive X-ray microanalyser
TOA	Thermal-optical carbon analyser
TSP	Total suspended particles
UNECE	United Nations Economic Commission for Europe
UP	Unpublished data and results (described in section 3)
VI	Virtual impactor
VOC	Volatile organic compound
WSOC	Water-soluble organic carbon
ZAF	Atomic number, absorption and fluorescence

1. INTRODUCTION

1.1 Aerosol particles and their impacts

Aerosol particles are liquid or solid particles suspended in the atmosphere. Their size varies from ~0.001 to ~100 μm. The particles are either injected directly into the atmosphere (primary particulate matter, i.e. primary PM) or they are formed from precursor gases in the atmosphere through gas-to-particle conversion processes (secondary PM). They originate from both natural and anthropogenic emission sources. On a global scale, the most significant sources of aerosols are windblown sea spray and soil dust, emissions from biological sources, volcanoes, combustion of fossil and biofuels, open biomass-burning fires and various industrial processes. The emission rates of particles and their precursor gases as well as meteorological conditions vary widely in different regions and seasons (Fig. 1 summarizes the major processes and impacts related to aerosols). Consequently, the concentrations and compositions of aerosols vary strongly in space and time (Tanré et al., 2001; Kaufman et al., 2002; Prospero et al., 2002; Dentener et al., 2006b; Kaufman and Koren, 2006; Tsigaridis et al., 2006; van der Werf et al., 2006; Koch et al., 2007) because the residence time of particles in the atmosphere is only an order of hours to weeks, depending mainly on the particle size and meteorological conditions.

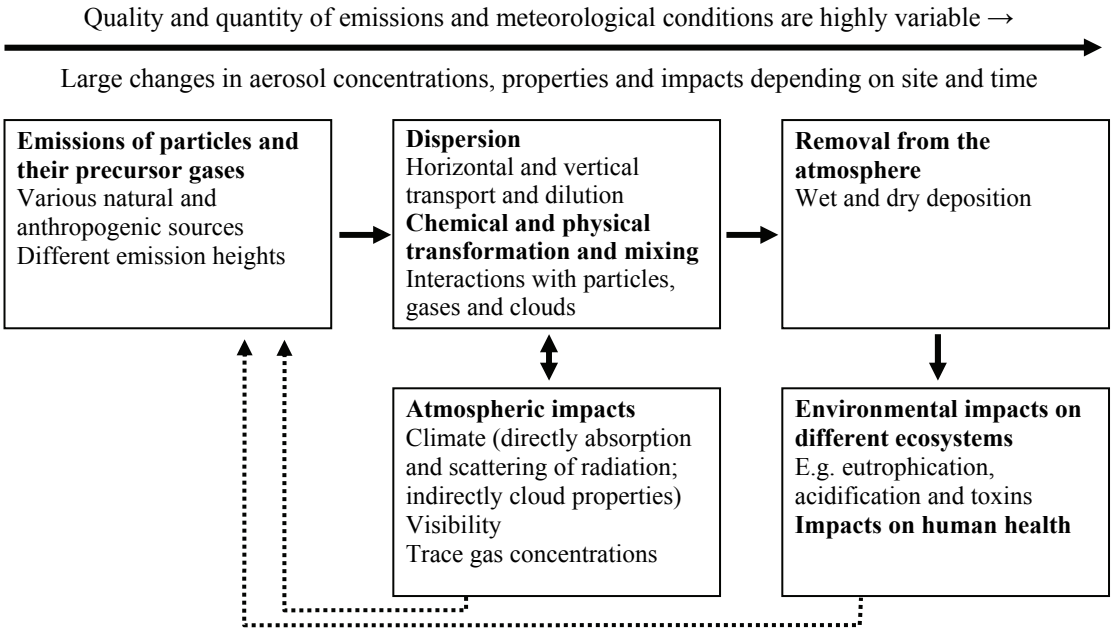

Figure 1. Schematic view of the main processes and impacts related to the long-range transport of aerosols.

The composition and mass concentrations of particles are substantially affected by long-range transport (LRT: distance from hundreds to thousands of kilometres), especially in areas with low local emissions (Stohl, 2006; Law and Stohl, 2007). In particular, aerosols in the fine size fraction ($PM_{2.5}$: particle diameter D_p < 2.5 μm) may be transported long distances before their removal from the atmosphere due to wet or dry deposition on the earth's surface. During transport and aging of aerosols, particles of different origin may alter their properties due to various physical and chemical conversion processes such as coagulation, condensation, chemical reactions with gases and cloud processes (Seinfeld and Pandis, 1998). The transformation processes may affect the composition, mixing state, concentration and size of different particle types. These are essential factors related to the environmental and health impacts of aerosols.

Particles are associated with various environmental impacts and they cause detrimental health effects in humans. In the atmosphere, they have both direct and indirect effects on climate, which affect both temperature and precipitation patterns on the earth's surface (Intergovernmental Panel of Climate Change (IPCC) 2001; 2007). The total net effect of particles is cooling. Particles also serve as chemical media for different reactions of gases in the atmosphere, which can decrease the concentrations of several trace gases, such as ozone (O_3), nitrogen oxides (NO_x) and sulphur dioxide (SO_2) (Crutzen and Arnold, 1986; Crutzen and Andreae, 1990; Dentener et al., 1996; Andreae and Crutzen, 1997; Dentener et al., 2006c). The transport and deposition of aerosols convey different chemical components (e.g. nutrients, acids and toxins) to various continental and marine ecosystems, which can cause, inter alia, eutrophication, acidification and toxic impacts (e.g. Ryther and Dunstan, 1971; Vanbreemen et al., 1982; Martin et al., 1994; European Commission, 2005a; Dentener et al., 2006a; EMEP, 2006b). PM also soils and corrodes technical materials and cultural heritage objects (e.g. Working Group on Effects, 2004; Bonazza et al., 2005). When particles are deposited in the lungs they can cause detrimental health effects, especially fine particles, the concentration of which is associated with increased morbidity and mortality (e.g. Pope and Dockery, 2006; WHO, 2006a, b).

1.2 Aerosol emissions and fine particle concentrations in Finland

On a global scale, the anthropogenic emissions of particles and their precursor gases have increased strongly during the last 250 years due to the Industrial Revolution and the huge increase in the human population (van Aardenne et al., 2001; Mouillot and Field, 2005; Dentener et al., 2006b; Junker and Liousse, 2006; Mouillot et al., 2006; Stier et al., 2006; Tsigaridis et al., 2006). During the coming decades, their emissions are also projected to remain high or to decrease slowly, depending on the scenario assumptions (Streets et al., 2004; Dentener et al., 2006c; Stier et al., 2006). The warming climate may also alter the emissions from natural sources (Tegen et al., 2004; Tao and Jain, 2005; Woodward et al., 2005; Mahowald et al., 2006a, 2006b, 2006c; Stier et al., 2006). However, past and future developments in anthropogenic and natural aerosol emissions and concentrations have varied and will vary in different regions. For instance in most Western European countries, the anthropogenic emissions of particles and their precursor gases are now declining (European Commission, 2005a; EMEP, 2006a, b; WHO, 2006b; Kupiainen and Klimont, 2007).

In Finland, anthropogenic emissions of fine particles and their precursor gases are low compared with the more polluted regions of Europe (EMEP, 2006a, b). Even in the urban areas of Helsinki, 50-70% of the $PM_{2.5}$ mass originates from LRT (Vallius et al., 2003; Karppinen et al., 2004; Kauhaniemi et al., 2007). In general, $PM_{2.5}$ concentrations are also low in Finland; the mean $PM_{2.5}$ concentrations in 1999-2001 were only 9.6 μg m^{-3} at an urban traffic site (Vallila) in Helsinki and 5.8 μg m^{-3} at a rural background site (Hyytiälä) in southern Finland (Laakso et al., 2003). However, the particle concentration and composition vary substantially, depending on meteorological conditions and aerosol source regions. High particle mass concentrations are observed when air masses arrive from the polluted continental areas of Eastern and central Europe, and low concentrations when aerosols originate from the direction of the Atlantic and Arctic oceans (Pakkanen et al., 2001b; Ricard et al., 2002; Ruoho-Airola et al., 2004; Sogacheva et al., 2005; Tunved et al., 2005; Niemi et al., 2006a). During the strongest LRT pollution episodes, the 24-h mean particle mass concentrations multiply compared with the annual mean levels, and the WHO guideline value (25 μg m^{-3}) for 24-h $PM_{2.5}$ mean concentrations is exceeded.

1.3 Objectives of the study

In this thesis, the sources and physicochemical properties of LRT aerosols were investigated (1) in southern Finland during selected LRT pollution episodes and unpolluted periods and (2) over the Atlantic Ocean between Europe and Antarctica during a voyage. Furthermore, a long-term (8 years) examination of LRT episode frequency in southern Finland was performed. Before the studies of this thesis, the sources and composition of particles had been examined only during a few LRT episodes in Finland (Tervahattu et al., 2002a, 2002b, 2004). In general, the composition of aerosol particles has been studied mostly with bulk chemical methods at various continental and marine sites. In this thesis, individual particle and bulk chemical analyses were used together with remote-sensing results to obtain a comprehensive view of the LRT of aerosols. In particular, electron microscopy with elemental analysis was used to provide information on the chemical composition, sources, morphology and mixing state of individual particles.

The aim of this thesis was to determine the impact on air quality by pollution episodes of LRT aerosols. This main objective was divided into the following research questions concerning different aspects of LRT aerosols in Finland and over the Atlantic Ocean.

1. How often does LRT cause pollution episodes of fine particles in southern Finland?
2. Which are the main sources of particles during LRT episodes in southern Finland?
3. How do particle mass and number concentrations change in different size fractions during LRT episodes in southern Finland?
4. How do the composition and origin of *individual* particles change during polluted and unpolluted LRT periods in southern Finland?
5. How does LRT of aerosols from continental sources affect the composition of *individual* coarse particles over the Atlantic Ocean between Europe and Antarctica?

This thesis consists of four published articles and some unpublished results. The main research objectives of each paper and the purposes of the unpublished data and results are summarized at the beginning of section 3.

2. THEORETICAL BACKGROUND

2.1 Particle size distribution and modes

Aerosols are suspensions of solid or liquid particles in a gas. In the case of atmospheric aerosols, this gas is air. The diameter of aerosol particles (D_p) varies between ~0.001 and ~100 μm. In the lower size limit, particles are formed by small molecular clusters, and the upper limit is caused by rapid sedimentation of large particles. Since particle diameter and mass can vary about five and eight orders of magnitude, respectively, particle size is the most important parameter for characterising the behaviour of aerosols. The shape and density of particles in the atmosphere are not uniform, which prevents unique definitions of particle size. Therefore, the size of particles is usually measured in terms of some equivalent diameter that is dependent on a physical or geometrical property. *Number size distributions* are often measured based on the *electrical mobility* of particles in an electrical field. To determine particle *mass size distribution*, particles are usually separated into several size fractions based on their *aerodynamic diameter*. The aerodynamic diameter is defined as the diameter of a unit density (1 g cm^{-3}) sphere having a terminal settling velocity equal to that of the given particle. *Geometric sizes* and shapes of particles can be measured using optical and electron microscopes.

In the atmosphere, the particle size distributions are not uniform but particles are concentrated into certain size ranges called modes. The size distribution can often be presented in terms of four modes: the nucleation ($D_p < 0.025$ μm), Aitken ($0.025 < D_p < 0.1$ μm), accumulation ($0.1 < D_p < 1$ μm) and coarse ($D_p > 1$ μm) particle mode (Fig. 2). Since the size distributions are highly variable in time and space, the size limits of modes and sometimes even the number of modes differ in various environments. The modality in size distributions is caused by several factors; (1) particle source and formation mechanisms (particle formation from hot or low-volatility vapours or from mechanical processes), (2) physicochemical processes during transport (coagulation, condensation, evaporation, interphase reactions occurring on the particle surface or inside particles and cloud processes) and (3) removal mechanisms (dry deposition due to diffusion, sedimentation, impaction and interception as well as wet deposition due to washout and rainout).

The nucleation mode particles are emitted directly into the atmosphere from combustion sources due to condensation of supersaturated hot vapours or they are formed in the atmosphere at ambient temperature due to gas-to-particle conversion of low-volatility vapours (e.g. sulphuric acid H_2SO_4, water, ammonia NH_3 and some organic compounds) (Seinfeld and Pandis, 1998; O'Dowd et al., 2002; Kulmala, 2003, 2004). The residence time of nucleation mode particles in the atmosphere is short (~ minutes to hours) because they rapidly attain larger sizes due to rapid coagulation of nucleation mode particles with each other (self-coagulation) or with larger particles and due to condensation of vapours on their surfaces (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000; Kulmala et al., 2004).

The Aitken mode particles originate either directly from the emissions of combustion sources (e.g. small soot particles) or they are formed in the atmosphere due to coagulation and condensation growth of nucleation mode particles. The Aitken mode particles can continue growing to accumulation mode size due to coagulation and condensation as well as to cloud processes. Since particles larger than ~40-120 nm can act as cloud condensation nuclei (CCNs) (Komppula et al., 2005; Dusek et al., 2006), cloud processes can force the large Aitken mode particles to grow into the accumulation

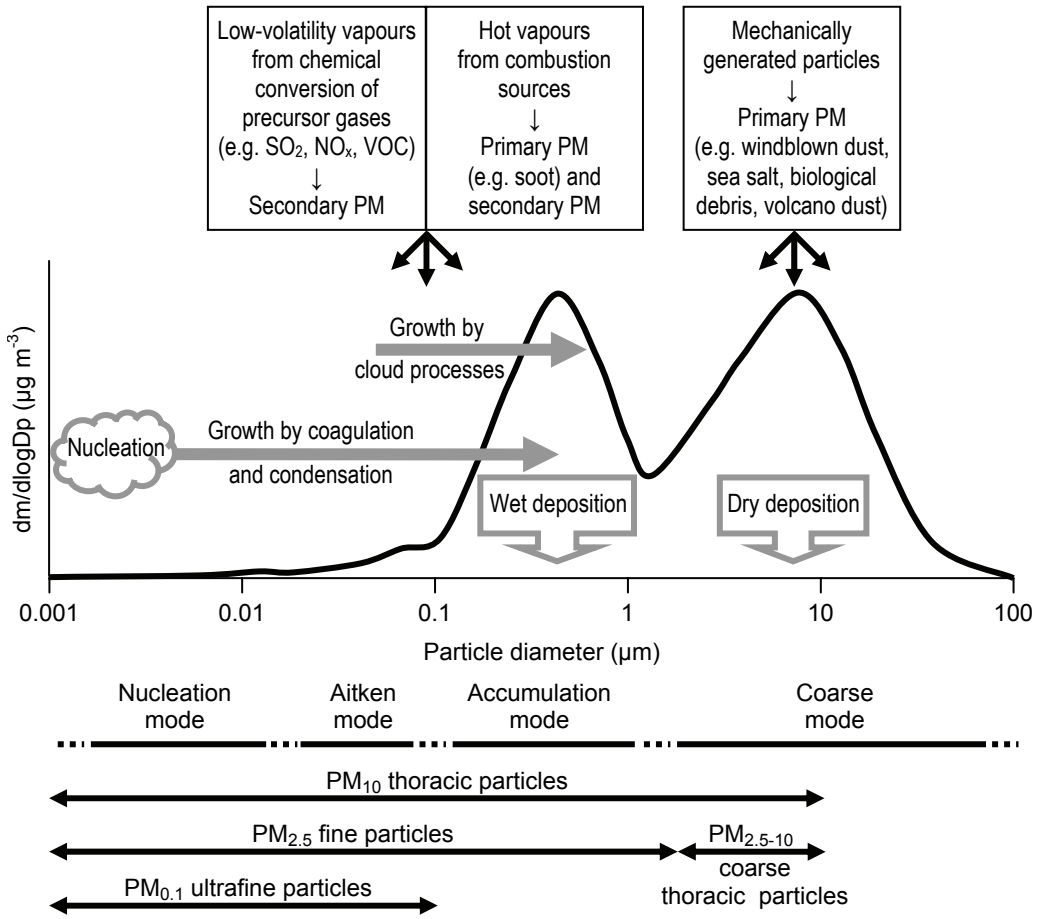

Figure 2. Schematic mass size distribution of particulate matter. Principle modes, sources and particle formation, growth and removal mechanisms are indicated.

mode size fraction and increase the size of accumulation mode particles. Cloud droplets (typical diameters ~5-100 µm) provide a medium with large surface area and liquid volume, in which some gaseous species can be readily dissolved and oxidized (e.g. SO_2 → sulphate SO_4^{2-}) (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). When the droplets evaporate, the residue particles are larger than the original CCNs due to additional oxidized PM. Furthermore, the size of particles can be increased due to chemical reactions of gases on cloud droplet surfaces, to coalescence of cloud droplets with each other and to impaction of particles into the cloud droplets.

The accumulation mode particles are either formed in the atmosphere due to growth processes of Aitken mode particles or they are emitted directly to the atmosphere from burning sources (e.g. large soot particles and small fly ash particles) and to some extent also from mechanical processes, although most of the mechanically formed particle mass belongs to the coarse mode size range. The most fundamental size limit related to sources, processes and properties of aerosols is division between *fine* (includes nucleation, Aitken and accumulation modes) and *coarse particles* (includes coarse mode). The dividing limit between fine and coarse size fractions varies in different studies (also in this work) depending on the focus and methodology of research. For instance, the division limit is often 2.5 µm in health-oriented studies and 1 µm in climate-oriented studies. In this work, various size fractions of fine and coarse particles were studied, and the following terminology was selected; fine particles usually refer to $PM_{2.5}$ and in some cases also to submicron (D_p < 1 µm) size fractions (mentioned in the text) while coarse particles refer to all supermicron (D_p > 1 µm) size fractions studied

(e.g. $PM_{1\text{-}3.3}$, $PM_{3.3\text{-}11}$). Fine submicron particles are mainly formed directly in burning processes or indirectly through gas-to-particle conversion processes. Most of them do not usually grow into the coarse size fraction, because the growth processes are quite inefficient for larger particles, due to their low surface-to-volume ratio. *The particles in coarse mode* originate mainly from different mechanical processes such as grinding, wind or erosion. The coarse mode consists of windblown soil dust, road dust, sea-salt particles (SSPs) from sea spray, particles from living or dead biological organisms and volcanoes.

The modality of particle size distributions is also regulated by different deposition mechanisms, because their efficiency varies strongly depending on particle size. In *dry deposition*, particles collide with the earth's surface. It removes coarse particles most rapidly because sedimentation and inertial impaction are most efficient for that size fraction. For Aitken and nucleation mode particles, diffusion is the most important dry deposition mechanism. There is no efficient dry deposition mechanism for accumulation mode particles, as the mode name already suggests. They are mostly removed by *wet deposition*, either in washout (particles already inside the rain droplets or ice crystals in cloud) or in rainout (particles collide and coalesce with droplets or ice crystals below clouds). The typical atmospheric residence time is from days to weeks for accumulation mode particles and from minutes to days for coarse mode particles.

Most of the particle mass concentration is either formed by accumulation mode or coarse mode particles in the atmosphere, depending on the site. *Ultrafine particles* ($PM_{0.1}$ = nucleation + Aitken mode particles) rarely account for more than a few percent of the total particle mass concentrations, due to their small size (Seinfeld and Pandis, 1998). The surface area of particles is usually largest in the accumulation mode size fraction (Seinfeld and Pandis, 1998). Very high number concentrations of nucleation mode particles are observed in the immediate vicinity of combustion sources (e.g. busy traffic sites and fresh industrial plumes), but their concentrations decrease rapidly when the distance from the emission sources increases (Laakso et al., 2003; Kulmala et al., 2004; Pirjola et al., 2006). Therefore, the long-term mean concentration levels of nucleation mode particles are usually low in clean background areas. However, high concentration peaks of nucleation mode particles are observed due to local/regional nucleation burst events (Laakso et al., 2003; Kulmala et al., 2004). During LRT of aerosols, the relative proportion of particles in the accumulation mode increases, because the ultrafine particles grow into the accumulation mode size range and because the deposition efficiency is lowest for accumulation mode particles.

2.2 Chemical components in particles and their sources

The chemical compositions of fine and coarse particles differ substantially because their main sources and formation pathways are different. The major components in the fine size fraction are inorganic ions (sulphate SO_4^{2-}, nitrate NO_3^- and ammonium NH_4^+), carbonaceous materials (organic carbon (OC) and elemental carbon (EC)) and aerosol-bound water. Soil-derived mineral particles, sea salt, biogenic organic materials (e.g. pollen, spores, plant and animal debris), NO_3^- and aerosol-bound water are typical components in coarse particles. The main sources and formation pathways as well as typical chemical forms for the major constituents of aerosol particles are summarized in the following sections.

2.2.1 Secondary inorganic ions

The major secondary inorganic ions in aerosol particles are SO_4^{2-}, NO_3^- and NH_4^+. They are all formed in the atmosphere from their precursor gases (e.g. SO_2, NO_x and NH_3) to a great extent. SO_4^{2-} has also a large primary source, i.e. sea salt.

The major precursor gases for *SO_4^{2-} formation* in the atmosphere are SO_2 and dimethyl sulphide (DMS; CH_3SCH_3) (Berglen et al., 2004). SO_2 originates mostly from anthropogenic sources (especially from fossil fuel burning), but volcanoes are also a significant source. The main source of DMS is marine plankton. Furthermore, minor amounts of other reduced S-containing precursor gases (e.g. hydrogen sulphide H_2S, carbon disulphide CS_2, carbonyl sulphide OCS and methyl mercaptan CH_3SH) are released from both natural and anthropogenic sources. DMS and other reduced precursors can be oxidized (e.g. by OH and NO_3) to SO_2 in the atmosphere. The SO_2 is oxidized to SO_4^{2-} in the aqueous phase (e.g. by hydgrogen peroxide H_2O_2 and O_3), gas phase (e.g. by OH) or on particle surfaces (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000; Berglen et al., 2004; Zuberi et al., 2005). The gas-phase reactions produce H_2SO_4, which posseses a very low saturation vapour pressure and can readily either nucleate (new particle formation) or condense onto pre-existing particles. The SO_4^{2-} formation rates in the atmosphere are controlled by several factors, including concentrations of oxidants, concentration ratios with other air pollutants, acidity of the liquid water associated with particles and relative humidity (RH). On a global scale, the aqueous-phase formation for SO_4^{2-} is the dominant (~80%) pathway (Berglen et al., 2004).

The most important precursor for *NO_3^- formation* in the atmosphere is nitric acid (HNO_3), which is an oxidation product of nitrogen dioxide (NO_2). The main sources of NO_2 and its precursor nitric oxide (NO) are fossil fuel and biomass burning, soil microbial activity and lightning (Jaeglé et al., 2005; Muller and Stavrakou, 2005). These oxidation reactions involving NO_2 to HNO_3 occur in the gas phase, aqueous phase and on particle surfaces (Dentener and Crutzen, 1993; Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000; Metzger et al., 2002; Schaap et al., 2004). HNO_3 readily adsorbs onto surfaces, particularly if there is water on the surface, and it easily dissolves in clouds and fogs.

The precursor for *NH_4^+ formation* in the atmosphere is NH_3, which is the only significant gaseous base in the atmosphere. The main sources of NH_3 are excretions of domestic animals, fields (especially due to use of synthetic nitrogen fertilizers), biomass burning and oceans (Bouwman et al., 1997). NH_3 reacts readily with acid aerosol particles, forming different compounds with SO_4^{2-} (e.g. ammonium bisulphate $(NH_4)HSO_4$, letovicite $(NH_4)_3H(SO_4)_2$ and ammonium sulphate $(NH_4)_2SO_4$)) and with NO_3^- (e.g. ammonium nitrate NH_4NO_3).

The relative proportions of different NH_4^+, NO_3^- and SO_4^{2-} compounds in particulate form are dependent on several factors, such as the amounts of their precursor gases in the atmosphere, RH and temperature (Ansari and Pandis, 1998; Seinfeld and Pandis, 1998; Metzger et al., 2002; Schaap et al., 2004; Vayenas et al., 2005). NH_3 first neutralizes H_2SO_4 to form $(NH_4)_2SO_4$. The remaining (excess) NH_3 may form NH_4NO_3, as shown in the following reaction:

$$HNO_3\,(g) + NH_3(g) \leftrightarrow NH_4NO_3\,(s,aq) \qquad \text{(Reaction 1)}$$

In high summer temperatures, NH_4NO_3 concentrations are low because it is thermodynamically unstable (new NH_4NO_3 formation is suppressed and previously formed NH_4NO_3 evaporates) (Feng and Penner, 2007). NO_3^- and SO_4^{2-} precursor gases (e.g. HNO_3, H_2SO_4 and SO_2) may also react with SSPs and mineral particles, which is the most important formation pathway for NO_3^- and SO_4^{2-} in the coarse size fraction (see sections 2.2.3 and 2.2.4).

2.2.2 Carbonaceous components

Carbonaceous aerosol components form a large but highly variable proportion of atmospheric aerosols. This fraction may contain thousands of different chemical compounds (e.g. n-alkanes, n-alkanoic acids, polycyclic aromatic hydrocarbons (PAHs), dicarboxylic acids, amino acids and saccharides). Usually only a small fraction of these compounds can be identified with current analysis methods (Rogge et al., 1991, 1998; Simoneit et al., 2004). Traditionally the total carbon (TC) content of PM is defined as the sum of all carbon contained in the particles, except in the form of inorganic carbonates (CO_3^{2-}) (Pöschl, 2005; Fuzzi et al., 2006). TC can be divided into EC and OC. OC can be further divided by its sources or chemical properties into several classes (e.g. primary vs. secondary sources and water-soluble vs. water-insoluble fractions).

EC is emitted directly into the atmosphere from various combustion sources (e.g. fossil fuel and biofuel combustion and open biomass-burning fires) (Lighty et al., 2000; Bond et al., 2004). It is emitted as soot particles, which are formed of numerous spherical particles (diameter ~20-50 nm) (Seinfeld and Pandis, 1998; Lighty et al., 2000; Kis et al., 2006). The morphology of soot varies from short chains to complex chain-agglomerates. The internal microstucture of soot is layered and formed by graphene-like sheets mixed with minor amounts of other compounds. Soot contains mainly C but also small quantities of H and traces of other elements. Furthermore, soot particles adsorb OC compounds when the combustion products cool down. EC strongly absorbs light, and so has also been referred to as black carbon (BC). The terms EC, BC and soot are often used interchangeably; however, they are usually measured with different analysis methods, each of which has its own emphasis on the results. Soot often refers to measurements with morphological detection (e.g. electron microscopy), EC is usually analysed based on the thermochemical properties of particles (e.g. thermo or thermo-optical methods), while BC measurements stress light-absorbing properties (e.g. optical methods). Furthermore, some organic compounds are also quite heat-resistant and absorb light ('brown carbon' = light-absorbing carbonaceous components other than soot; e.g. tarry materials from burning, soil humic acids, humic like substances and bioaerosols), which further complicates direct comparability and interpretation of EC, BC and soot measurements (Hand et al., 2005; Pöschl, 2005; Andreae and Gelencser, 2006; Bond and Bergstrom, 2006; Graber and Rudich, 2006).

OC is operationally defined as the difference between TC and EC (OC = TC – EC). OC, TC, and EC are usually analysed with thermal or thermo-optical methods and the C content is determined as carbon dioxide (CO_2) or methane (CH_4), depending on the method. The division between OC and EC is dependent on the methods and procedures selected. The OC fraction is formed of hundreds of different organic compounds. A large proportion of these compounds (~20-60% of the OC mass) are water-soluble (WSOC = water-soluble organic carbon) (Pöschl, 2005). In addition to C, OC compounds contain variable amounts of other elements (e.g. O, H, N). Therefore, the original mass of the organic matter (OM) is often estimated using conversion factors. Typical conversion factors used are ~1.4-1.8 for (fresh) urban OC and ~ 1.9-2.3 for

(aged and more oxidized) rural OC (Turpin et al., 2000; Turpin and Lim, 2001; Pang et al., 2006). Aerosols heavily impacted by wood smoke can have even higher conversion factors (2.2-2.6) (Turpin and Lim, 2001).

OM originates from various natural and anthropogenic activities. It can be divided into primary and secondary organic aerosols (POAs and SOAs). *POAs* can enter the atmosphere in many ways, including particles from open biomass burning, fossil fuel combustion, residential wood combustion, refuse incineration, meat cooking, biological sources (e.g. plant debris, plankton debris, pollen, fungal spores, bacteria and viruses), organic soil dust and organic road dust components (e.g. asphalt bitumen, tyre and brake abrasion) (Jacobson et al., 2000; Seinfeld and Pankow, 2003; Bond et al., 2004; O'Dowd et al., 2004; Sun and Ariya, 2006). POA emission rates are especially high in tropical areas due to open biomass burning and in urban/polluted areas due to fossil fuel and biofuel burning (Bond et al., 2004; Dentener et al., 2006b).

SOA components are formed by chemical reactions (oxidation) and gas-to-particle conversion of volatile organic compounds (VOCs) in the atmosphere, which may proceed through different pathways: (1) new particle formation: formation of semivolatile organic compounds (SVOCs) by gas-phase reactions and participation of the SVOCs in the nucleation and growth of new aerosol particles; (2) gas-particle partitioning: formation of SVOCs by gas-phase reactions and uptake (adsorption or absorption) by pre-existing aerosol or cloud particles; (3) heterogeneous or multiphase reactions: formation of low-volatility or nonvolatile organic compounds by chemical reaction of VOCs or SVOCs at the surface or in the bulk of aerosol or cloud particles (Pöschl, 2005; Fuzzi et al., 2006). On a global scale, biogenic VOCs (especially terpenes from plants) are the predominant source of SOA, whereas in polluted areas anthropogenic VOCs (especially combustion sources) can be important precursors (Tsigaridis and Kanakidou, 2003; Kanakidou et al., 2005; Henze and Seinfeld, 2006; Tsigaridis et al., 2006). The SOA formation rates are still poorly quantified, but SOAs can form at least 50% of the total OM on a global scale (Tsigaridis and Kanakidou, 2003; Kanakidou et al., 2005; Tsigaridis et al., 2006).

2.2.3 Sea salt

Seawater droplets are ejected into the atmosphere due to wind-induced wave breaking and bubble bursting (Leifer et al., 2000, 2006; Mårtensson et al., 2003; Leifer and de Leeuw, 2006). When water evaporates from sea-spray droplets, the remaining salts form liquid or solid SSPs, depending on the RH. Fresh SSPs contain the same ions present in seawater, especially inorganic ions (e.g. Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+ and CO_3^{2-}) and variable minor amounts of organic soluble and insoluble materials (Duarte and Cebrian, 1996; Middlebrook et al., 1998; Finlayson-Pitts and Pitts, 2000; O'Dowd et al., 2002; Tervahattu et al., 2002b; Volkman and Tanoue, 2002; Zhang et al., 2003b; Cavalli et al., 2004).

Sea salt reacts with acidic gases in the atmosphere, which results in Cl^- release and substitution by other anions. The most important substituting anions are SO_4^{2-} and NO_3^- which can be formed from the oxidation of different N- (e.g. HNO_3, NO_2 and dinitrogen pentoxide N_2O_5) and S-containing (e.g. SO_2 and H_2SO_4) gases (Kerminen et al., 1998; Laskin et al., 2003; Rossi, 2003; Gibson et al., 2006b; Virkkula et al., 2006b). The simplified net reactions of sea salt with HNO_3 and H_2SO_4 are shown below.

$$NaCl(s,aq) + HNO_3(g) \rightarrow NaNO_3(s,aq) + HCl(g) \qquad \text{(Reaction 2)}$$

$2NaCl(s,aq) + H_2SO_4(g) \rightarrow Na_2SO_4(s,aq) + 2HCl(g)$ (Reaction 3)

In clean regions above or near the sea, Cl^- depletion by organic acids (e.g. with methane sulphonic acid CH_3SO_3H which originates from oxidation of DMS or with dicarboxylic acids) may also be significant (Kerminen et al., 1998). The reaction rate of sea salt with gaseous compounds is highest when sea salt occurs in liquid form due to high RH (ten Brink, 1998; Saul et al., 2006). The loss of Cl^- from SSPs can be calculated based on the Cl/Na ratio of seawater. This ratio decreases due to release of hydrogen chloride (HCl) and other Cl-containing gases.

Ion ratios of sea water are often utilized to calculate the non-sea-salt (nss) fractions of ions after bulk chemical analysis of aerosol samples. For instance, the proportion of non-sea-salt sulphate ($nss\text{-}SO_4^{2-}$) can be calculated based on the following equation: $[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - 0.246 \times [Na^+]$. This method may give estimates that are too high for $nss\text{-}SO_4^{2-}$ if the proportion of Na from continental sources is high (e.g. waste burning and certain minerals, Ooki et al., 2002). Nss-fractions can also be calculated for other typical sea-salt ions (e.g. Mg^{2+}, Ca^{2+} and K^+).

2.2.4 Mineral particles

Windblown soil dust is the principal source of mineral particles in the atmosphere. Dust source regions include mainly deserts, dry lake beds and semiarid desert fringes but also areas in drier regions where vegetation has been reduced or soil surfaces have been disturbed by human activities (Pye, 1987; Prospero et al., 2002; Engelstaedter et al., 2006; Moulin and Chiapello, 2006). Occasionally volcanic eruptions produce large amounts of mineral dust (Pye, 1987). In urban areas, road dust is a significant source of mineral particles (Pakkanen et al., 2001b; Kupiainen and Tervahattu, 2004; Putaud et al., 2004; Tervahattu et al., 2006). Furthermore, fly ash particles from combustion sources (especially from coal burning) are sometimes classified as mineral particles when they mainly contain mineral material residues of fuels. Submicron-sized fly ash particles are formed through the vaporization-nucleation-condensation pathway, while supermicron-sized fly ash particles are formed from residual materials of fuel that have remained in a solid or liquid phase throughout combustion (Lighty et al., 2000; Kutchko and Kim, 2006).

Soil dust particles contain various minerals of the earth's crust, including quartz, feldspars, carbonates (e.g. calcite and dolomite) and clays (e.g. illite, kaolinite, chlorite, montmorillonite/smectite). The most common elements are O, Si, Al, Fe, Ca, Mg, Na, K and Ti. The mineral and elemental composition of particles varies, depending on the source regions of particles (Chiapello et al., 1997; Claquin et al., 1999; Goudie and Middleton, 2001; Krueger et al., 2004; Ro et al., 2005; Arimoto et al., 2006).

Mineral particles react readily with gas-phase compounds during transport, especially when the RH is high (Al-Hosney and Grassian, 2005; Vlasenko et al., 2006). Furthermore, mineral particles can also be mixed with other particle types through coagulation and cloud processes. Thus, several chemical components (e.g. NO_3^-, SO_4^{2-}, NH_4^+ and Cl^--compounds) were observed on the surfaces of LRT mineral dust particles (Sullivan et al., 2007). CO_3^{2-} minerals are especially susceptible to reaction with acidic gases because CO_3^{2-} can be substituted by the anions of stronger acids (Laskin et al., 2005b; Hwang and Ro, 2006b). Different reaction mechanisms of carbonates and other minerals with gaseous N (e.g. HNO_3 and N_2O_5) and S (e.g. SO_2 and H_2SO_4) compounds are not yet totally understood (Usher et al., 2003a, b; Al-Hosney and Grassian, 2005;

Gibson et al., 2006b; Zhang et al., 2006). However, the simplified net reactions of calcite ($CaCO_3$) with HNO_3 (Al-Hosney and Grassian, 2005; Kelly and Wexler, 2005; Gibson et al., 2006b; Hodzic et al., 2006) and H_2SO_4 (Dentener et al., 1996; Zhuang et al., 1999; Al-Hosney and Grassian, 2005; Li et al., 2006) are shown below as examples:

$CaCO_3(s,aq) + 2HNO_3(g) \rightarrow Ca(NO_3)_2(s,aq) + CO_2(g) + H_2O(g,aq)$ (Reaction 4)
$CaCO_3(s,aq) + H_2SO_4(g) \rightarrow CaSO_4(s,aq) + CO_2(g) + H_2O(g,aq)$ (Reaction 5)

2.2.5 Trace metals

Aerosols often contain variable minor amounts of different trace metals (e.g. V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Ba and Pb). Their total proportion in particle mass is usually a few percent or less. They originate from various sources, including the metal industry, fossil energy production, refuse incineration and traffic (Pakkanen et al., 2001a, b; Vallius et al., 2005; Finnish Environment Institute, 2006; Grieshop et al., 2006; Ragosta et al., 2006; Murphy et al., 2007).

2.2.6 Particle-bound water

The water content of particles can vary strongly, depending on particle composition and RH. The ability of particles to take up water is termed *hygroscopicity*. In general, inorganic salts and water-soluble organic compounds are hygroscopic, while fresh soot and mineral particles are hydrophobic. However, the hydrophobic particles are converted to more hygroscopic forms during transport, due to condensation of hygroscopic compounds, coagulation with more hygroscopic particles and to chemical reactions occurring on the surface or in the interior of particles (Rudich, 2003; Usher et al., 2003a; Krueger et al., 2004; Maria et al., 2004; Zuberi et al., 2005; Petters et al., 2006). Most aerosol particles are hygroscopic and water vapour can be adsorbed on the surface of the particles or absorbed into the bulk of the particles. For particles consisting of water-soluble material, the uptake of water can lead to aqueous droplet formation.

The composition of salts and organic compounds significantly affects the hygroscopicity of particles and their growth rates due to water uptake. Inorganic salt-containing particles are usually solid at very low RH. However, when the RH increases, they spontaneously begin to absorb water and form aqueous droplets. This phase-transition RH is called the *deliquescence relative humidity* (DRH). Further increase in RH leads to additional water condensation and particle growth. The decrease in RH causes evaporation of water and particles crystallize at a certain RH, which is called the *efflorescence relative humidity* (ERH). ERH is lower than DRH and this phenomenon is called *hysteresis*. For instance, DRH and ERH are 75% and 45%, respectively, at 25 °C for NaCl (Biskos et al., 2006). Thus, particles may be crystalline or aqueous at a given RH, depending on the RH history. The deliquescence and efflorescence points are characteristic for each salt and are usually lower for salt mixtures than for pure compounds (Seinfeld and Pandis, 1998). The organic particles that are formed by water-soluble compounds are usually less hygroscopic than inorganic salt particles (Hansson et al., 1998; Virkkula et al., 1999; Cruz and Pandis, 2000; Mochida and Kawamura, 2004; Carrico et al., 2005; Badger et al., 2006; Svenningsson et al., 2006; Varutbangkul et al., 2006). They do not always have a clear DRH point and hysteresis is rarely observed (Kanakidou et al., 2005).

Particles larger than ~40-120 nm can be activated as *CCNs* when water vapour is supersaturated over the particle. Typical values of supersaturation are about 0.2-2% in

clouds and 0.02-0.2% in fogs (Finlayson-Pitts and Pitts, 2000). The RH needed for activation of particles as CCNs is dependent on particle size (Kelvin's effect) and composition (Raoult's effect); large and hygroscopic particles can act as CCNs in the lowest supersaturations (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). Thus, the hygroscopicity of particles decreases their residence time in the atmosphere, because they are more easily removed due to rainout wet deposition.

Aerosol particle mass concentrations are usually presented as dry mass, which is often measured at 50% RH. Since several inorganic salts display hysteresis, the mass concentration results depend on which side the stabilization RH (50%) is approached from. Therefore, the amount of aerosol-bound water is difficult to measure. In Europe, the proportion of aerosol-bound water was estimated to be ~10-35% of the PM_{10} and $PM_{2.5}$ concentrations at 50% RH and ~20ºC temperature (Hueglin et al., 2005; Tsyro, 2005). Since the fine particles more often contain hygroscopic materials than the coarse particles, the proportion of water is higher in the fine size fraction.

2.2.7 Mixing state

The mixing state of aerosol particles describes how various chemical components are located among the particles. Knowledge of the mixing state of particle populations is critical, because the mixing state affects the chemical and optical behaviour of particles. The terms internal and external mixture are used to describe two extremes of the mixing state. If the selected chemical components are found in the same particles, they are *internally mixed*. If they are located in separate particles, they are *externally mixed*.

The mixing state of various chemical components can be studied, using individual particle analysis methods. In off-line methods, particle samples are collected first and analysed later (e.g. by electron microscopy coupled with elemental analyses or by different mass spectrometry methods) (McMurry, 2000; Sipin et al., 2003; Szaloki et al., 2004; Laskin et al., 2006). In on-line methods, particles are analysed in real-time (e.g. by different mass spectrometry methods) (Sipin et al., 2003; Sullivan and Prather, 2005; Murphy et al., 2006; Nash et al., 2006). As described in the previous sections, mixing of different chemical components increases during transport, due to chemical and physical transformation pathways (e.g. coagulation, condensation, evaporation, interphase reactions occurring on the particle surface or inside the particles, and cloud processes). Primary particles can be internally mixed with other primary particle types (e.g. mixing of sea salt, mineral particles and soot) and with secondary particle mass (e.g. SO_4^{2-}, NO_3^-, NH_4^+ and OC compounds) (Andreae et al., 1986; Pósfai et al., 1999; Ro et al., 2001; Laskin et al., 2002, 2005a; Zhang et al., 2003a; Hara et al., 2005; Johnson et al., 2005; Dall'Osto and Harrison, 2006; Kojima et al., 2006; Sullivan et al., 2007; Vester et al., 2007). Secondary chemical components can form various particle types and their mixtures, depending on their emission rates and meteorological conditions (e.g. different mixtures of SO_4^{2-}, NO_3^-, NH_4^+ and/or OC compounds) (Sullivan and Prather, 2005; Tolocka et al., 2005; Dall'Osto and Harrison, 2006; Murphy et al., 2006). Furthermore, the composition of the particle core and surface layer may differ strongly, due to surface-active compounds (Russell et al., 2002; Tervahattu et al., 2002b, 2005; Peterson and Tyler, 2003; Donaldson and Vaida, 2006).

2.3 Emissions and transport of particles

2.3.1 Aerosol emissions in Europe

In most regions of continental Europe, the emissions of aerosol particles and their precursor gases originate mainly from anthropogenic sources such as traffic, energy production, industry and domestic combustion (EMEP, 2006a, b; WHO, 2006b). All precursor gases are currently controlled by international agreements, the UNECE (United Nations Economic Commission for Europe) Convention on Long-range Transboundary Air Pollution (EMEP, 2006b) and the European Union's National Emission Ceilings Directive (2001/81/EY). Their anthropogenic emissions were ~14 000, ~16 000, ~6 000 and ~14 000 Gg a^{-1} for SO_2, NO_x, NH_3 and VOCs, respectively, in 2004. Their emissions will continue decreasing due to agreed legislation (EMEP, 2006a). Primary PM_{10} and $PM_{2.5}$ emissions were ~5 000 and ~3 000 Gg a^{-1} in 2004 (EMEP, 2006a). Their emissions are also decreasing in most regions (WHO, 2006b; Kupiainen and Klimont, 2007) and there are plans to include PM in future international protocols (e.g. European Commission, 2005b). In Finland, the anthropogenic primary PM_{10} and $PM_{2.5}$ emissions were ~60 and ~40 Gg a^{-1}, respectively, in 2004 (EMEP, 2006a).

The emission inventories are still quite inaccurate for some anthropogenic source types (e.g. road dust emissions from traffic, emissions from domestic wood combustion and emissions from agriculture and forestry) (EMEP, 2006a; WHO, 2006b; Karvosenoja et al., submitted 2007). The emission estimates for natural sources (e.g. dust from arid regions, biological particles and sea salt) and for open biomass burning are especially uncertain (Andreae and Merlet, 2001; EMEP, 2006a; WHO, 2006b; Niemi, 2007). Furthermore, the secondary formation rates of organic PM are poorly quantified (Kanakidou et al., 2005; EMEP, 2006a; Fuzzi et al., 2006; WHO, 2006b). The emission rates of particles and their precursor gases also vary widely in time and space. The uncertainties in aerosol emissions and processes make the source apportionment of ambient PM challenging. Various particle types from anthropogenic and natural sources may be transported long distances and elevate particle concentrations far from they sources.

2.3.2 Transport distance

The transport distance of particles is strongly dependent on particle size and meteorological conditions. As mentioned earlier, particles in the accumulation mode size fraction can remain for long periods (~days-weeks) under dry conditions in the atmosphere. Typically, they undergo LRT from hundreds to thousands of kilometres. The residence time of coarse particles in the atmosphere is usually from minutes to days and they usually originate mostly from local sources, at distances of hundreds of metres to tens of kilometres. However, the smallest (~1-5 μm) coarse particles may also travel quite long distances, if they are ejected into high altitudes, because their gravitational settling velocities are not very high. For instance, the settling velocities for particles with aerodynamic diameters of 1, 3, 5, 10 and 100 μm are 3, 25, 67, 262 and 21 514 m d^{-1}, respectively (Hinds, 1999). Coarse particles can be lifted to high altitudes (from hundreds of metres to several kilometres) by strong winds (e.g. desert duststorms) or by high-temperature plumes (e.g. open biomass-burning fires and volcanoes) (Goudie and Middleton, 2001; Dentener et al., 2006b).

2.3.3 High particle concentration episodes

The particle concentrations may rise to extraordinarily high levels due to LRT (= *LRT episode*) when air masses arrive during suitable meteorological conditions (no rain and weak mixing of air masses) from regions with very high emissions of particles and/or their precursor gases (Fisher et al., 2005; Kukkonen et al., 2005). The *local-scale episodes* (e.g. episodes due to wintertime inversions, resuspension of road dust, emissions from stationary emission sources and large-scale fireworks) and regional-scale *photochemical pollution episodes* (common in warm and hot regions such as Southern Europe) are excluded in this work because it is focused on the LRT of fine particles in Northern Europe and coarses particle over the Atlantic Ocean. However, LRT episodes can occur at the same time with the episodes caused by local emissions, which complicates the source identification of particles, especially in urban areas (Fisher et al., 2005; Kukkonen et al., 2005, 2007; Aarnio et al., 2007; Baklanov et al., 2007). Since there can be strong and rapid changes in local and regional meteorological conditions (e.g. atmospheric stability, inversions, wind direction and rain) as well as in emissions (e.g. wildfire emissions and dust resuspension), it is still difficult to provide reliable forecasts for both local-scale and LRT episodes (Fisher et al., 2005; Kukkonen et al., 2005; Baklanov et al., 2007).

On a global scale, the most common particle sources of LRT episodes are strongly dependent on season and region but they can be roughly divided into three major types and their mixtures (based on numerous scientific articles during the last 10 years): (1) open biomass-burning fire events, (2) desert duststorms and (3) emissions from heavily polluted areas due to anthropogenic activities (e.g. bio- and fossil fuel burning and industrial activities). Biological particles (e.g. pollen) and sea salt can also sometimes elevate particle concentrations far from their sources (Tervahattu et al., 2002a; Sofiev et al., 2006a). Furthermore, volcanic eruptions can cause high particle concentrations at high altitudes.

Open biomass burning is a major source of particles on a global scale (Crutzen and Andreae, 1990; Andreae and Merlet, 2001; Bond et al., 2004; Dentener et al., 2006b; van der Werf et al., 2006; Niemi, 2007). Part of the biomass is burned, due to natural fires which are mainly caused by lightning (Food and Agricultural Organization (FAO) 2001). However, most open biomass-burning fires are caused by human activity, either intentionally or accidentally (FAO, 2001). Most open biomass burning occurs in the tropics (especially in Africa, South and Central America, Southeast Asia and Oceania), but agricultural waste burning and wildfires are also common in several temperate and boreal regions during the warm season (FAO, 2001; Bond et al., 2004; Hoelzemann et al., 2004; Ito and Penner, 2004; Carmona-Moreno et al., 2005; van der Werf et al., 2006; Niemi, 2007). Therefore, strong particle episodes from open biomass burning are observed annually in every continent (excluding the polar regions).

Soil dust emissions are concentrated in the arid and semiarid regions of the globe. The strongest dust source is the Sahara Desert (Arimoto, 2001; FAO, 2001; Goudie and Middleton, 2001; Engelstaedter et al., 2006). The Sahara and Gobi deserts and the area between them are called the ‘dust belt’, because the emissions of dust are very high throughout the region (Prospero et al., 2002). Near these regions, strong dust storm episodes are frequently observed during dusty seasons. Duststorm particles can be transported very long distances at lower concentrations. For instance, Saharan dust is frequently transported over the Mediterranean to Southern Europe (Ryall et al., 2002; Escudero et al., 2007), over the Atlantic Ocean to America (Arimoto, 2001; Goudie and

Middleton, 2001; Reid et al., 2003; Riemer et al., 2006) and rarely even over the Pacific Ocean to America (McKendry et al., 2007). Asian dust transport to America is also frequently observed (VanCuren and Cahill, 2002; Fairlie et al., 2007).

Pollution plumes from anthropogenic sources (e.g. energy production, industry, traffic and residential burning) in industrialized regions may cause high particle concentrations far from the source areas. They can also be transported between continents as lower concentrations and the potential need for hemispheric reduction targets is under international discussion even for air pollutants with quite short (~ over 1 week) residence time (Holloway et al., 2003; Damoah et al., 2004; Hadley et al., 2007; Stohl et al., 2007b; Task Force on Hemispheric Transport of Air Pollution, 2007). High particle concentration peaks are observed in clean continental areas around the polluted areas and over the oceans near polluted regions. For instance, aerosol plumes from polluted areas of Europe, Eastern Asia and western USA are transported long distances around surrounding continental and marine areas (Tanré et al., 2001; Kaufman et al., 2002; Quinn and Bates, 2005; Stohl et al., 2007b).

2.3.4 Source identification methods

The source identification of LRT particles is challenging because they may originate from various sources and their composition may change substantially during transport. Furthermore, particles from local sources are also mixed with the same aerosols and their contribution may be difficult to separate from that of LRT aerosols. In the source analysis of aerosols, the following information is often used: chemical composition of particles, dispersion modelling results of aerosols and their precursors, and aerosol-monitoring measurement data from the earth's surface or from space with satellite instruments.

The amounts and ratios of different chemical components in particles vary significantly, depending on their emission sources. Each source has a characteristic *chemical emission profile* for primary particles and for precursor gases of secondary particles (Watson et al., 2001). In long-term source identification studies, the source apportionment of particles at a study site is often performed using receptor models, such as chemical mass balance models (a priori information on the chemical emission profiles of each source is needed) or multivariate statistical models (Seinfeld and Pandis, 1998; Watson et al., 2002; Yli-Tuomi et al., 2003).

Chemical tracer compounds are especially useful for source identification, because they mainly originate from a given source (Simoneit, 2002). An excellent tracer is source-specific (no other significant sources), quantitative (about the same proportion in emissions regardless of differences in source types and formation processes) and stable during transport (no decomposition or secondary formation). In practice, tracers do not usually fulfil these requirements perfectly, but they may still provide valuable semiquantitative information. For instance, levoglucosan is a unique organic tracer compound for biomass-burning aerosols, because it is a thermal breakdown product of cellulose (Simoneit et al., 1999). However, the proportion of levoglucosan in biomass-burning aerosols is strongly dependent on the burning conditions and quality of the biomass burned, which restricts its use as a quantitative tracer compound (Hedberg and Johansson, 2006; Mazzoleni et al., 2007). Furthermore, recent studies have indicated that some decomposition of levoglucosan may occur under some conditions during LRT (Saarnio et al., 2006), although levoglucosan was considered quite a stable molecule in previous studies (Fraser and Lakshmanan, 2000; Jordan et al., 2006). The simultaneous

use of chemical emission profiles and several tracer compounds may provide more reliable results (Hedberg and Johansson, 2006; Ward et al., 2006; Mühle et al., 2007). For instance, the traditional tracers of biomass-burning aerosols are high concentrations and proportions of K and OC in the fine size fraction (Andreae, 1983; Andreae and Merlet, 2001).

Chemical source apportionment is often complemented with *aerosol source area analysis* to determine the most significant emission source regions (e.g. Yli-Tuomi et al., 2003; McMeeking et al., 2006). One traditional way to examine potential source areas is to calculate *backward air mass trajectories*. The backtrajectories show the arrival routes (directions) of air parcels in at a given site but not the distances at which the most significant emissions have occurred or potential wet deposition during transport. *Backward (inverse) dispersion modelling* is a more advanced method in order to estimate potential sources areas because it provides probability maps of source areas and potential wet deposition can also be included in calculations (Saarikoski et al., 2007). *Forward dispersion modelling methods* are often utilized to obtain more detailed information on the potential sources, because their results show how aerosols (or other pollutants) are transported from various emission sources under ambient meteorological conditions (Hongisto and Sofiev, 2004; Sofiev et al., 2006b; Saarikoski et al., 2007; Stohl et al., 2007a). However, forward dispersion modelling requires detailed time- and space-resolved emission inventory and meteorological data, which are not available for all regions and source types.

In most recent studies, direct *satellite detections* of aerosols have been used to estimate the level of aerosol emissions and their transport from different source types to distant regions. Satellite instruments measure the emissions of selected wavelengths of electronmagnetic radiation arriving from the earth. Various disturbances in the atmosphere (e.g. amounts of particles, trace gases and clouds) or on the earth's surface (e.g. fire hotspots, changes in land and vegetation cover and changes in ocean surface properties such as photosynthetic activity or temperature) cause changes in radiation intensities. Satellite remote-sensing methods have been used to describe emissions and dispersion of aerosols and to separate their major components (e.g. mineral dust, smoke or pollution) (e.g. Tanré et al., 2001; Kaufman et al., 2002; Ichoku et al., 2004; Kaufman and Koren, 2006; van der Werf et al., 2006). Since the presence of clouds disturbs aerosol measurements by satellites, results are mostly available for periods without cloud cover. The spatio-temporal cover of satellite measurements is also always limited due to selected orbits. Furthermore, the satellite data interpretation and calculation of quantitative estimates are subject to various limitations. For instance, the emissions from open biomass burning can be estimated based on the amounts of active fire hot spots or fire scars but the total amount of biomass burned and the following emission estimates are still quite inaccurate, especially for regions with poorly detected smouldering peat fires or surface fires under tree cover (Kasischke and Penner, 2004; van der Werf et al., 2006; Niemi, 2007).

2.4 Environmental and health effects

Aerosol particles have numerous impacts on the environment. They can transport various chemical components long distances before they are deposited in different ecosystems. Depending on the chemical composition of the particles, they can cause acidification, eutrophication and toxic effects (e.g. Ryther and Dunstan, 1971; Vanbreemen et al., 1982; Kauppi et al., 1990; Martin et al., 1994; Dentener et al., 2006a; EMEP, 2006b). PM also soils and corrodes technical materials and cultural

heritage objects (e.g. Working Group on Effects, 2004; Bonazza et al., 2005). Particle deposition in the lungs causes detrimental health effects (e.g. Dockery et al., 1993; Pope and Dockery, 2006; WHO, 2006a, b). Particles in the atmosphere reduce visibility, alter the concentrations of certain trace gases and affect the climate through impacts on radiative balance and the hydrological cycle (e.g. Crutzen and Arnold, 1986; Crutzen and Andreae, 1990; Charlson et al., 1992; Dentener et al., 1996; Andreae and Crutzen, 1997; IPCC, 2007). Since the spectrum of different impacts is so diverse, only some of the aspects related to climate and health impacts are shortly summarized below.

2.4.1 Climate change

The global mean surface temperature has increased 0.74 °C (90% confidence limits from 0.56 to 0.92 °C) during the last 100 years, according to the latest report of the IPCC (IPCC, 2007). This is mainly caused by anthropogenic greenhouse gases, such as CO_2, CH_4, nitrous oxide (N_2O), certain halocarbons and O_3. Their concentrations have increased strongly compared with preindustrial time (year 1750) (IPCC, 2007). At the same time, human activity has also increased the concentrations of aerosol particles in the atmosphere (IPCC, 2001; Dentener et al., 2006b; Tsigaridis et al., 2006), which has a net cooling effect on climate (IPCC, 2007). *Radiative forcing* is used as a measure of the warming or cooling influence that a factor has on the energy balance in the earth-atmosphere system. The radiative forcing of the above-mentioned greenhouse gases from anthropogenic emissions was estimated to be approximately +3.0 W m^{-2} in year 2005 compared with preindustrial times (year 1750), while the corresponding coarse estimate for atmospheric aerosol particles is -1.2 W m^{-2} (IPCC, 2007). Thus, aerosol particles have counteracted the warming caused by greenhouse gases (Andreae et al., 2005; Mishchenko et al., 2007; Wild et al., 2007). Since the residence time of particles is on the order of 1 week in the atmosphere, the effects of aerosols on different climate parameters (e.g. temperature and precipitation) are highly variable in different regions and seasons (IPCC, 2001; Tanré et al., 2001; Kaufman et al., 2002; Bellouin et al., 2005; Kaufman and Koren, 2006; Schulz et al., 2006; Storelvmo et al., 2006).

The radiative forcing of aerosols can have direct and indirect effects. Particles have a *direct effect* on radiative forcing because they scatter and absorb solar and infrared radiation in the atmosphere. The *indirect effect* refers to the changes in cloud properties due to aerosols. Particles can act as CCNs that increase the concentrations of cloud droplets but decrease their mean size. This change increases cloud albedo (the first indirect or cloud albedo or Twomey effect: Twomey, 1974) and cloud lifetime (the second indirect effect: Albrecht, 1989). Both indirect effects increase the reflection of solar radiation back to space. The anthropogenic radiative forcing caused by the direct effect was estimated to be -0.5 W m^{-2} (90% confidence limits from -0.9 to -0.1 W m^{-2}) in year 2005 compared with year 1750, while the corresponding estimate for the first indirect effect is -0.7 W m^{-2} (90% confidence limits from -1.8 to -0.3) (IPCC, 2007). The reliability of estimates for direct and especially for indirect effects are still very low, due to a low level of scientific understanding (Lohmann and Feichter, 2005; Yu et al., 2006; IPCC, 2007). The second indirect effect (cloud lifetime) is not yet included in the above-mentioned estimates by the IPCC due to difficulties in measuring or modelling it reliably, but it was estimated to be from -0.3 to -1.4 W m^{-2} (Lohmann and Feichter, 2005).

The concentration, size, composition, mixing state and shape of particles determine their climatic impacts. The most significant cooling aerosol types are SO_4^{2-}, (non-light-absorbing) OC, NO_3^- and sea salt (IPCC, 2001; Satheesh and Moorthy, 2005; Schulz et

al., 2006). The radiative forcing of mineral dust is still poorly quantified and even the sign of direct radiative forcing is still uncertain (IPCC, 2001) although it may be slightly negative (Balkanski et al., 2007). Dust not only scatters and absorbs solar radiation but also absorbs and emits outgoing longwave radiation (IPCC, 2001; Satheesh and Moorthy, 2005; Engelstaedter et al., 2006). Furthermore, mineral dust particles are often coated with hygroscopic material during transport (Dentener et al., 1996; Matsuki et al., 2005; Hwang and Ro, 2006b; Kojima et al., 2006; Sullivan et al., 2007), which increases their chances of acting as CCNs, but their indirect radiative forcing is also poorly quantified (IPCC, 2001; Bauer and Koch, 2005).

Soot is the most important light-absorbing particle type, and causes positive radiative forcing (IPCC, 2001; Satheesh and Moorthy, 2005). The light absorption efficiency of soot particles increases strongly when they are internally mixed with SO_4^{2-} or OC compounds (Jacobson, 2001; Chung and Seinfeld, 2005; Schnaiter et al., 2005; Bond et al., 2006). Since absorption of solar radiation by soot causes heating of the atmosphere, it can result in evaporation of cloud droplets, which is termed a semidirect climate effect of aerosols (Ackerman et al., 2000; Johnson et al., 2004; Koren et al., 2004; Lohmann and Feichter, 2005; Jacobson, 2006). Furthermore, soot particles increase the absorption of light on the surface of snow, which results in positive radiative forcing (Warren, 1982; Jacobson, 2004; IPCC, 2007).

2.4.2 Health effects

Numerous epidemiological and toxicological studies have shown during the last 15 years that aerosol particles smaller than 10 μm in diameter (PM_{10} = thoracic particles) cause detrimental health effects (Dockery et al., 1993; Pope and Dockery, 2006). The particles of the fine size fraction ($PM_{2.5}$) are considered to be more dangerous to health than those of the coarse thoracic size fraction ($PM_{2.5\text{-}10}$) (Laden et al., 2000; WHO, 2003, 2006b; Pope and Dockery, 2006). Both short- and long-term exposure to fine particles causes increased morbidity and mortality of persons with cardiopulmonary diseases (Pope and Dockery, 2006). Long-term exposure to current ambient $PM_{2.5}$ concentrations may lead to a marked reduction in life expectancy, primarily due to increased cardiopulmonary and lung cancer mortality (Pope et al., 2002; Pope and Dockery, 2006). For instance, the recent estimate by the WHO for the LRTAP Convention and the European Commission's Clean Air for Europe (CAFE) programme suggests that the mean statistical lifetime expectancy was reduced by 9 months, due to ambient fine particles in the 25 members states of the European Union (EU) in year 2000 (European Commission, 2005a; WHO, 2006b). Although the particles in the $PM_{2.5\text{-}10}$ size fraction are not as detrimental to health as are fine particles, they are nevertheless also associated with increased morbidity and hospital admissions of persons with respiratory diseases (Brunekreef and Forsberg, 2005; Pope and Dockery, 2006).

Since the composition, size and shape of particles are dependent on their sources and conversion processes occurring during transport, the health effects of various particle types may differ strongly (Salonen et al., 2000; Brunekreef and Forsberg, 2005; Jalava et al., 2006; Pope and Dockery, 2006). Currently, fine particles from combustion sources are considered to be the most dangerous to health (Laden et al., 2000; Penttinen et al., 2004; Pope and Dockery, 2006). Fine particles can be inhaled deep into the lungs (alveolar region) and particles from combustion sources contain abundant toxic compounds, including heavy metals and carcinogenic PAHs (Lighty et al., 2000; Pope and Dockery, 2006). However, there is a lack of quantitative information on the types of

sources (e.g. various fossil fuels and biofuels are burned under different conditions) causing the most dangerous particle emissions and how significantly the aging of particles alters their toxic properties. Since the source-specific health risks of aerosols are still insufficiently known, it is difficult to define the most cost-effective measures to reduce the emissions of particles and their precursor gases (European Commission, 2005a; Forsberg et al., 2005; WHO, 2006b; Kennedy, 2007).

Epidemiological studies of large populations have been unable to identify any threshold concentration below which particles have no effect on health (Pope and Dockery, 2006). The recent WHO guideline values of PM_{10} mass concentrations are 20 μg m^{-3} for annual mean and 50 μg m^{-3} for 24-h mean (WHO, 2006a). The corresponding values for $PM_{2.5}$ mass concentrations are 10 and 25 μg m^{-3}. The current PM_{10} limit values for the EU are clearly higher than the WHO guidelines: 40 μg m^{-3} for annual mean and 50 μg m^{-3} for 24-h mean (35 exceeded days allowed per year) (directive 1999/30/EY). The $PM_{2.5}$ standards are under construction in the EU, and the European Commission has proposed 25 μg m^{-3} as an annual ceiling value for the entire EU (European Commission, 2005b). The EU also regulates the concentrations of some toxic components of PM. The annual limit value for Pb concentration is 0.5 μg m^{-3} (directive 1999/30/EY). The EU also aims to reduce carcinogenic health risks of heavy metals (As, Cd and Ni) and PAHs (benzo[a]pyrene) via recent directive (2004/107/EY), which contains the annual target concentrations in PM_{10} mass to be met by 2012.

3. MATERIALS AND METHODS

This thesis consists of four published articles and some unpublished results. The main research objectives of each paper and the purposes of the unpublished data and results are summarized below.

Article **I** describes an LRT pollution episode of particles in southern Finland on 17-22 March, 2002. The main objectives of the report were to identify the sources of the particles, to characterise particle composition and to examine changes in particle mass and number concentrations in different size fractions.

Article **II** describes three LRT pollution episodes of particles in southern Finland on 12-15 August, 26-28 August and 5-6 September, 2002. The aims of the report were the same as in article **I**.

Article **III** reports the chemical characteristics of aerosols at a rural background site (Hyytiälä) in southern Finland in May 2004 during an LRT pollution episode (PM_1 ~16 μg m^{-3}, backward air mass trajectories from the southeast), an intermediate period (PM_1 ~5 μg m^{-3}, backtrajectories from the northeast) and clean periods (PM_1 ~2 μg m^{-3}, backtrajectories from the northwest/north). The main objectives of the report were (1) to describe the composition, morphology and mixing state of individual aerosol particles in different size fractions ($PM_{0.2\text{-}1}$,$PM_{1\text{-}3.3}$ and $PM_{3.3\text{-}11}$), and (2) to identify particle sources during polluted and unpolluted LRT periods.

Article **IV** describes the composition of individual small-sized (D_p ~ 1-3 μm) coarse aerosol particles observed over the Atlantic Ocean between Europe and Antarctica during a voyage in November-December 1999. The main aim of the report was to investigate the impact of emissions from continental sources on aerosol composition over the ocean.

Unpublished results **UP** were used to describe the frequency and strength of LRT pollution episodes of fine particles ($PM_{2.5}$) in southern Finland during the period 1999-2006. The data and results are not published in peer-reviewed journals but most were shown in a Finnish report (Niemi et al., 2006a) and in an extended conference abstract (Niemi et al., 2006b). This work was initiated and planned by Niemi.

Five LRT episodes for in-depth studies in southern Finland are shown in a diagram at the beginning of the results (see section 4.1, Fig. 6). The materials and methods used for Articles **I** and **II** (four LRT episodes in 2002) and for the Unpublished results **UP** (LRT episode frequency in 1999-2006) are summarized in section 3.1. The corresponding information for Article **III** (an LRT episode and unpolluted periods in May 2004) is described in section 3.2. Finally, the material and methods for Article **IV** (coarse particles over the Atlantic Ocean) are shown in section 3.3.

3.1 LRT episodes of particles in southern Finland

The aerosol measurements (**I**, **II**, **UP**) are summarized in Table 1. The map of measurement sites is shown in Fig. 3. Since LRT episodes can occur at any day of the year, it was necessary to select results and samples that are available every day from ordinary air quality monitoring measurements. In general, this type of methodological combination is very useful in tracking LRT episode particles, because short-term measurement campaigns provide detailed information only for limited periods. The long-term monitoring measurements used here were performed in the Helsinki

Table 1. Summary of measurements at different sites for the in-depth studies of four LRT episodes in 2002 (**I, II**) and for the long-term episode frequency investigations in 1999-2006 (**UP**).

Analysed components analysis method, and time resolution		Helsinki Kallio	Helsinki Luukki	Helsinki Vallila	Imatra Mansikkala	Hyytiälä	Virolahti	Utö	Ähtäri
		Urban backg.	Rural backg.	Urban traffic	Urban traffic	Rural backg.	Rural backg.	Rural backg.	Rural backg.
• PM_{10} mass concentration with Eberline β-ray attenuation analysis	1 h	I, II	UP		II		II		
• $PM_{2.5}$ mass concentration with Eberline β-ray attenuation analysis	1 h	I, II, UP	UP						
• $PM_{>10}$, $PM_{2.5-10}$, $PM_{2.5}$ and PM_1 mass concentrations with gravimetric analysis	2-3 days					I, II, UP			
• Number concentrations in different size fractions with DMPS analysis[1]	15 min					I, II			
• SO_4^{2-}, (NO_3^-+HNO_3(g)) and (NH_4^+ + NH_3(g)) from TSP samples with IC analysis	1 day						I, II, UP	I, II, UP	I, II
• Elemental ratios of particles with SEM/EDX analysis [2]	1 day	I, II	I, II	I	II				

[1] Size fractions were nucleation (3-25 nm), Aitken (25-90 nm) and accumulation (90-500 nm) modes.
[2] Elemental ratios in individual particles and particle agglomerates were analysed for Na, Mg, Al, Si, S, Cl, K, Ca, Ti and Fe. $PM_{2.5}$ samples were analysed from Kallio and Vallila and PM_{10} samples from Luukki, Vallila and Mansikkala.

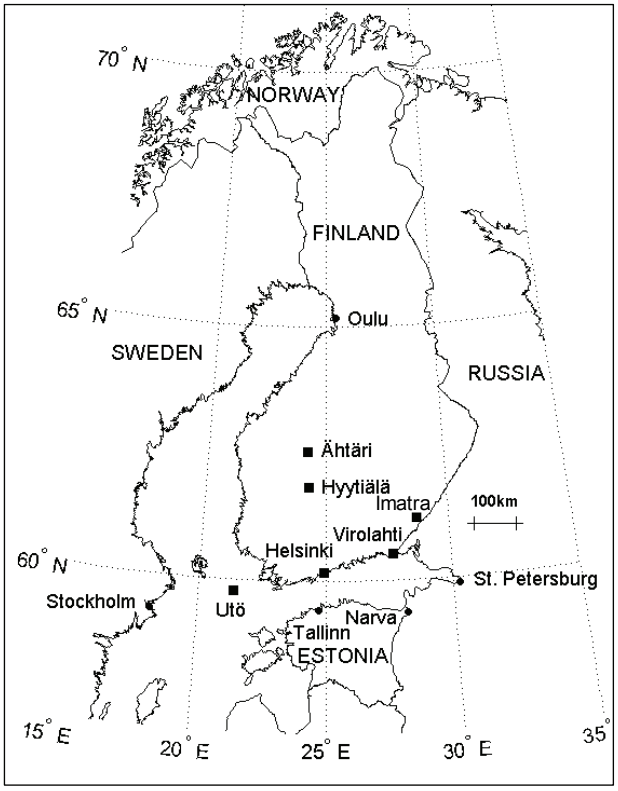

Figure 3. Locations of the measurement and sampling sites (marked with squares) in Finland (**II**).

metropolitan area by the Helsinki Metropolitan Area Council (YTV), in Imatra by the Imatra Environment Office, in Hyytiälä by the Department of Physical Sciences of the University of Helsinki, and in Utö, Virolahti and Ähtäri by the Finnish Meteorological Institute. Furthermore, air mass backward trajectories, fire detection from satellites and dispersion modelling results for smoke were used in source characterisation of aerosols (**I**, **II**). All materials and methods are shortly described in the following sections.

3.1.1 Particle mass and number concentration measurements

In this thesis, the PM_{10} and $PM_{2.5}$ mass concentration results from several monitoring sites in southern Finland were utilized to examine changes in particle mass concentrations due to LRT. The PM_{10} results from the Kallio and Luukki stations in the Helsinki metropolitan area, the Virolahti station, and the Mansikkala station in Imatra were used, as were the $PM_{2.5}$ results from Kallio and Luukki. All these measurements were performed using Eberline FH 62 I-R samplers (Eberline Instruments, Santa Fe, NM, USA) with PM_{10} or $PM_{2.5}$ inlets. The method is based on β-attenuation. The time resolution was 1 h.

The particle mass concentrations in different size fractions were measured at Hyytiälä (Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II)) station using a Dekati PM-10 three-stage impactor with a backup filter (Dekati Ltd, Tampere, Finland). The 50% aerodynamic cutoff diameters (D_{50}) of the impaction stages were 10, 2.5 and 1 μm. The collection substrates on the impaction stages were polycarbonate membranes with no holes (Nuclepore 800 203, diameter 25 mm; Whatman, Brentford, Middlesex, UK), and the backup filter material was made of Teflon with 2-μm diameter pore size (Gelman Teflo R2P J047, diameter 47 mm; Gelman Scientific Inc. (now Pall Corporation), East Hills, NY, USA). Smearing of substrates to prevent particles from bouncing back from the substrates and the gravimetric analysis are described in detail by Laakso et al. (2003). The time resolution was 2-3 d.

The particle number size distributions were measured in the diameter range between 3 and 500 nm, using a twin differential mobility particle sizer (DMPS) at Hyytiälä station. DMPS consists of a differential mobility analyser (DMA) and a condensation nucleus counter (CNC). It classifies particles into size classes, depending on the electrical mobility of the particles. The different size classes are separated by altering the voltage difference inside the DMA. The size distribution of the sampled aerosol population is then determined in the CNC, which counts the number concentration of every size class. The twin DMPS system used consisted of two different DMPSs: the first classified particles from 3 to 10 nm and the second particles from 10 to 500 nm. Both systems used Hauke-type DMAs (Winklmayr et al., 1991) and a closed-loop sheath flow arrangement (Jokinen and Mäkelä, 1997). The CNCs used were TSI Model 3025 and TSI Model 3010 in the first and second systems, respectively (Thermo Systems Inc., Scarborough, ME, USA). Before the size characterisation, the incoming aerosol was neutralized with a 2-mCi ^{85}Kr beta source. The time resolution was 10 min. The details of the DMPS sampling protocol are provided in Aalto (2001).

3.1.2 Bulk chemical analysis by IC

SO_4^{2-} , total nitrate (NO_3^- + HNO_3(g)) and total ammonium (NH_4^+ + NH_3(g)) are typical chemical components in LRT aerosols. Their concentrations were analysed with ion chromatography (IC; Dionex DX-500, Dionex Corporation, Sunnyvale, CA, USA; Waters, Waters Corporation, Milford, MA, USA). Daily total suspended particle (TSP) samples for IC analysis were collected in Ähtäri, Virolahti and Utö, using open-faced

two-stage filter packs (NILU Products AS; Norwegian Institue for Air Research, Kjeller, Norway) with cellulose filters (Whatman 40, diameter 47 mm). The details of the sampling and IC methods are described in Paatero et al. (2001).

3.1.3 Individual particle analysis by SEM/EDX

The elemental compositions of individual particles and agglomerates were studied using a scanning electron microscope (SEM - ZEISS DSM 962; Carl Zeiss, Oberkochen, Germany) coupled with an energy-dispersive X-ray microanalyser (EDX - LINK ISIS; Oxford Instruments, Tubney Woods, Abingdon, Oxfordshire, UK) with the atomic number, absorption and fluorescence (ZAF) correction measurement program. The daily $PM_{2.5}$ samples for SEM/EDX analysis were collected at Kallio and Vallila in the Helsinki metropolitan area. The PM_{10} samples were collected at Luukki in the Helsinki metropolitan area and at Mansikkala in Imatra. The particles were collected on fibreglass filter tapes (diameter of collection area spot ~ 1.5 cm), using Eberline FH 62 I-R samplers. In all, 25 particle samples (14 $PM_{2.5}$ and 11 PM_{10} samples) collected during four LRT episodes (17 and 19 March; 13 August; 27 and 28 August; 5 and 6 September 2002) and on reference days were selected for the analyses.

The samples were prepared for SEM/EDX analysis by pressing a two-sided sticky tape (Scotch Ruban Adhesive; 3M, St. Paul, MN, USA) attached to an aluminium plate on the filter surface covered with particles. The samples were then coated with C (Agar SEM Carbon Coater; Canemco and Marivac, Lakefield, Quebeck, Canada) to make the sample surfaces conductive. The SEM/EDX was operated at an accelerating voltage of 20 kV. The counting time of the X-ray spectrum was 15 s. The elemental compositions of 100 randomly selected particles or agglomerates (minimum diameter 1 μm) were analysed from each sample. Submicron-sized particles formed abundant large agglomerates during sampling and sample preparation for SEM/EDX analysis, enabling us to also obtain elemental information from the submicron size range by analysing these agglomerates. However, this agglomeration complicated detailed classification of the fine particle types, and thus only major differences in fine aerosols between episode and reference days could be observed (see the authors' response to the referees (**II**) from the website of Atmospheric Chemistry and Physics). The relative elemental weight percentages (normalized to 100%) were calculated using ZAF corrections for the following elements: Na, Mg, Al, Si, S, Cl, K, Ca, Ti and Fe. While the ZAF-corrected elemental results are semiquantitative for aerosol particles, the accuracy is sufficient to identify different particle types and to compare differences in elemental ratios of the same particle type in different samples (Gao and Anderson, 2001; Breed et al., 2002; Paoletti et al., 2002; Kupiainen et al., 2003).

3.1.4 Trajectories and dispersion of smoke

The potential source areas of LRT particles were investigated using backward air mass trajectories. The backtrajectories were produced using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Draxler and Rolph, 2003) with the Final Analyses (FNL) meteorological database at the National Oceanographic and Atmospheric Administration (NOAA) Air Resources Laboratory's web server (Rolph, 2003).

For detection of fire areas, daily active fire hotspot maps were used from Web Fire Mapper (http://maps.geog.umd.edu), which is part of the MODerate-resolution Imaging Spectroradiometer (MODIS) Rapid Response System (Justice et al., 2002). The Navy Aerosol Analysis and Prediction System (NAAPS) model results were used to

determine the distribution of smoke aerosols from fires (model description and results available from web pages of the Naval Research Laboratory, Monterey, CA, USA; http://www.nrlmry.navy.mil/aerosol/).

3.2 Polluted and unpolluted LRT periods in southern Finland

Aerosol sampling and measurements were performed at the Hyytiälä research station during a field campaign between 6 and 24 May 2004 (**III**). Detailed characterisation of individual particles with transmission electron microscopy (TEM) coupled with EDX microanalysis was performed for six sampling periods lasting 1-6 h. The main materials and methods used are summarized in Table 2. Furthermore, air mass backward trajectories, fire detection from satellites and dispersion modelling results for smoke were used in source characterisation of aerosols, similarly to those in section 3.1.4.

Table 2. Summary of measurements at Hyytiälä for in-depth studies during the LRT episode and unpolluted periods in May 2004 (**III**).

Analysed components and analysis method	Time resolution	Size fractions analysed
• Particle mass concentration with ELPI electrical impactor	10 min	PM_1
• Particle mass concentration with gravimetric analysis	2 days	$PM_{1.3}$ and $PM_{1.3\text{-}10}$
• OC and EC with TOC analysis	2 days	$PM_{1.3}$ and $PM_{1.3\text{-}10}$
• Ion concentrations (NO_3^-, SO_4^{2-}, Cl^-, MSA, oxalate, succinate, malonate, Na^+, NH_4^+,K^+, Mg^{2+} and Ca^{2+}) with IC analysis	2 days	$PM_{1.3}$ and $PM_{1.3\text{-}10}$
• Sum concentration of monosaccharide anhydrides (∑MA = levoglucosan + galactosan + mannosan) with LC/MS analysis	2 days	$PM_{1.3}$ and $PM_{1.3\text{-}10}$
• Morphology and elemental ratios of particles (elements with Z from C to Pb excluding N) with TEM/EDX analysis	1-6 h	$PM_{0.2\text{-}1}$, $PM_{1\text{-}3.3}$ and $PM_{3.3\text{-}11}$

3.2.1 Particle mass concentration measurements

The particle number concentrations and size distributions (from 29 nm to 10 μm) were monitored continuously during the field campaign (time resolution 1 s, averaged to 10 min) with an electrical low pressure impactor (Outdoor Air ELPI, Dekati Ltd). These results were used to calculate the PM_1 mass concentrations (equations shown in Saarikoski et al., 2005). Furthermore, the 2-d mean $PM_{1.3}$ and $PM_{1.3\text{-}10}$ mass concentrations were measured, using virtual impactor (VI) sampling and gravimetric analysis, as described in the next section.

3.2.2 Bulk chemical analysis by TOA, IC and LC/MS

Particle samples for bulk chemical analysis were collected with two identical VIs in parallel; one was used to collect samples for mass and ion analysis and the other for C analysis (Saarikoski et al., 2005). The VIs were modified versions of the original design of Loo and Cork (1988). They divide airborne PM into two size fractions: $PM_{1.3}$ and $PM_{1.3\text{-}10}$. The collection substrates for mass and ion analysis were Teflon filters (diameter 47 mm, pore size 3.0 μm; Millipore Fluoropore, Carrigtwohill, Cork, Ireland), while for C analysis quartz fibre filters were used (diameter 47 mm, Whatman QMA). In VI sampling for C analysis, denuders and backup filters were used to minimize sampling artefacts. The sampling time was 2 d.

The VI samples were analysed chemically for EC, OC, water-soluble ions and the sum of three monosaccharide anhydrides (∑MA = levoglucosan + galactosan + mannosan). The EC and OC were measured with the thermal-optical C analyser (TOA; Sunset

Laboratory Inc., Tigard, OR, USA). Ion analysis was performed using two Dionex-500 IC systems. The ions analysed were NO_3^-, SO_4^{2-}, Cl^-, methanesulphonate (MSA, $CH_3SO_3^-$), oxalate, succinate, malonate, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. The details of ion and C analysis, and also the weighting of VI samples to calculate particle mass concentrations, are described in Saarikoski et al. (2005). The ∑MA was determined, using a liquid chromatograph coupled with a mass spectrometer (LC/MS; Agilent 1100 Series, Trap SL; Agilent Technologies, Santa Clara, CA, USA). The analysis method is described in detail by Sillanpää et al. (2005).

3.2.3 Individual particle analysis by TEM/EDX

The morphology and elemental composition of individual aerosol particles were investigated using a Tecnai 12 TEM (FEI Company, Hillsboro, OR, USA) equipped with an EDAX EDX microanalyser (EDAX Inc., Mahwah, NJ, USA). The particle samples for TEM/EDX analysis were collected with a Battelle-type impactor (model I-1; PIXE International Corporation, Tallahassee, FL, USA), which is a modified version of the original design of Mitchell and Pilcher (1959). The Cu TEM grids (400-mesh) with carbon-coated Formvar films (Carbon Type-B, Ted Pella Inc., Redding, CA, USA) were placed on three impaction stages to collect particles in diameter ranges (cutoff sizes, D_{50}) of 0.2-1.0, 1.0-3.3 and 3.3-11 μm. The sample collection times were 1-6 h, depending on the particle concentrations during sampling. The TEM grids for six sampling periods (six periods and three size fractions, total 18 TEM grids) were used for TEM/EDX analysis.

The TEM was operated at an accelerating voltage of 120 kV and with a low beam current to minimize beam damage. The counting time for X-ray spectra was 20 live seconds. The minimum size of the particles analysed was 0.2 μm (geometric diameter). The elements analysed were with Z from C to Pb, excluding N. The X-ray counts from the carbon-Formvar coating (thickness listed as ~60 nm; contains abundant C, some O and minor amounts of Si) of the TEM grids were estimated by analysing the blank areas between particles. The net X-ray counts (= total counts – carbon-Formvar blank counts) of elements for each particle analysed were calculated, and their proportions were normalized to 100%. Although the elemental results were semiquantitative, the accuracy was sufficient to identify different particle types and to compare the differences in elemental ratios of the same particle type in different samples (Pósfai et al., 2003; Ebert et al., 2004; Ro et al., 2005; Laskin et al., 2006). The strong vacuum (~10^{-7} torr) and beam exposure causes evaporation of semivolatile compounds from particles. For this reason water, NH_4NO_3 and organic compounds with high vapour pressure were lost, as is typical in electron microscopy.

3.3 Coarse particles over the Atlantic Ocean between Europe and Antarctica

Aerosol measurements (**IV**) were taken over the Atlantic Ocean between Europe and Antarctica in November-December 1999 (Fig. 4a and b). Several properties of aerosols were investigated during the voyage. The particle number size distributions and concentrations were described by Koponen et al. (2002). The chemical mass concentrations and size distributions were analysed with bulk methods by Virkkula et al. (2006a; 2006b, in **IV** they are referred to as Virkkula et al. submitted for publication a and b). The composition of individual aerosol particles (**IV**) was investigated with the SEM/EDX method in the size range of ~1-3 μm, which is the fraction of coarse particles with the slowest removal from the atmosphere. Some bulk chemical results of Virkkula et al. (2006a; 2006b) were also used for comparison.

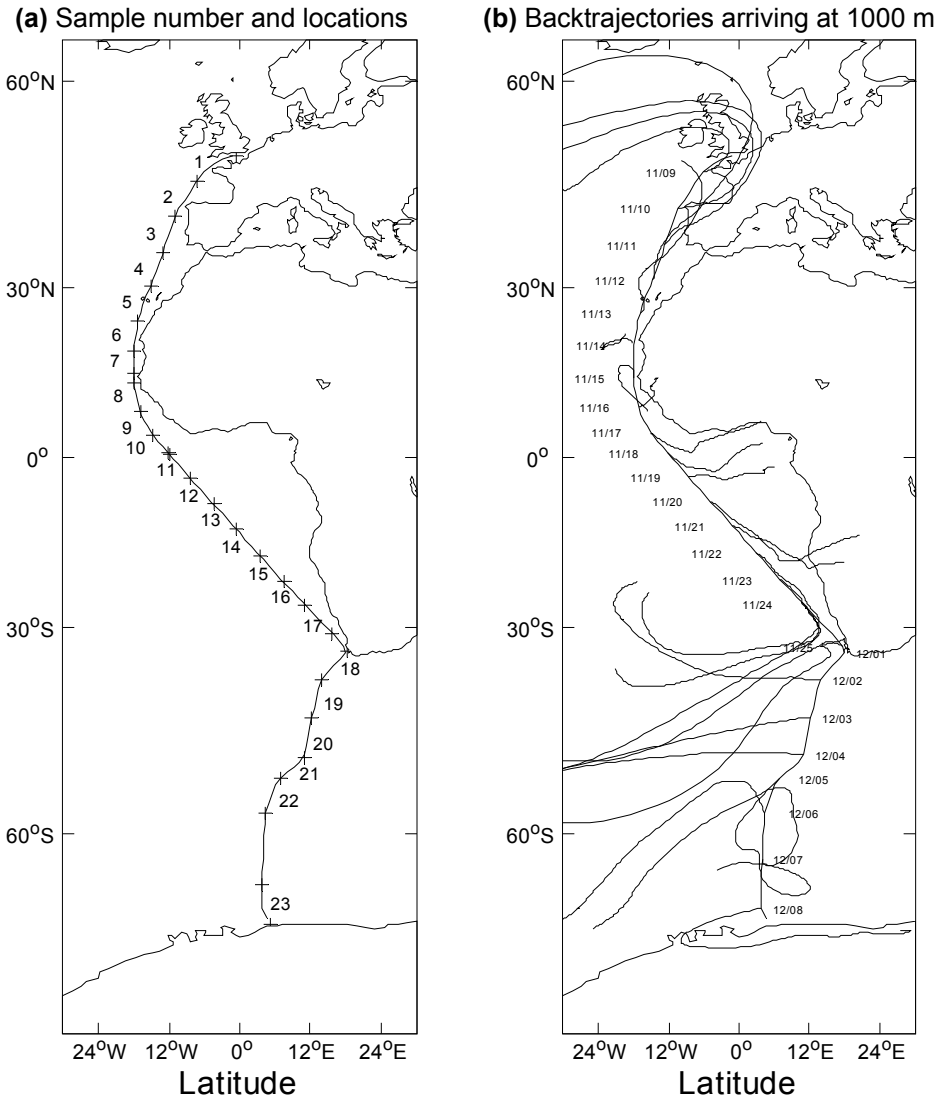

Figure 4. (a) Voyage route, locations of the sample changes (sample numbers 1-23) and **(b)** 5-day backward air mass trajectories arriving at the 1000-m level above the location of the ship between 9 November and 8 December 1999 (**IV**).

3.3.1 Individual particle analysis by SEM/EDX

The elemental composition of individual aerosol particles was investigated using the same SEM/EDX device and methodology as in **I** and **II** (described in section 3.1.3). The analysed elements (normalized to 100%) were Na, Mg, Al, S, Cl, K, Ca, Ti and Fe. The aerosol samples for SEM/EDX analysis were collected using a high-volume sampler with 240-mm quartz filters (Munktell MK 360; Cryo-Technik GmbH, Hamburg, Germany). The cutoff size (D_{50}) of the inlet was approximately 3 μm (Virkkula et al., 2006a) and the sampling time was 24 h. The number of particles investigated was 100 (samples 1-10 and 18) or 50 (samples 11-17 and 19-23) from each sample (see sample numbers in Fig. 4a).

3.3.2 Trajectories and dispersion of smoke and dust

The potential source areas of aerosols were investigated using HYSPLIT4 backward air mass trajectories. The NAAPS model results were used to examine dispersion of smoke and desert dust near the coast of Africa. The short description and references for the HYSPLIT4 and NAAPS models were shown in section 3.1.4.

4. RESULTS AND DISCUSSION

This part is presented in four sections. Section 4.1 gives an overview of the frequency and strength of the LRT episodes for fine particles in southern Finland, especially in the Helsinki metropolitan area, during 8 years in 1999-2006 (**UP**). The characterisation and source identification of particles during the four selected LRT episodes in year 2002 are presented in section 4.2 (**I**, **II**). Section 4.3 describes in detail the individual particle composition and sources of aerosols in southern Finland during an LRT pollution episode and during cleaner periods in May 2004 (**III**). Finally, section 4.4 focuses on individual particle composition and sources of coarse aerosol particles over the Atlantic Ocean between Europe and Antarctica during a voyage in November-December 1999 (**IV**).

4.1 LRT episode frequency of fine particles in southern Finland

LRT episodes of fine particles were detected, based on particle mass monitoring results in the Helsinki metropolitan area. During the LRT episodes, the particle mass concentrations rose simultaneously to extraordinarily high levels at every monitoring station, including the urban background station in Kallio and rural background station in Luukki (Fig. 5). The following concentration criterion was defined for the Kallio monitoring site as episodic (unusually) high concentration level: the 24-h $PM_{2.5}$ moving average concentration exceeded 25 µg m^{-3}, which is three times higher than the long-term mean concentration (8.6 µg m^{-3}) during 1999-2006. At Luukki, the $PM_{2.5}$ concentration was only measured in 2004-2006 and PM_{10} in 1999-2003. Therefore, the concentration criteria for LRT episodes were defined separately for both periods; 24-h moving average PM_{10} > 25 µg m^{-3} during the 1999-2003 episodes and $PM_{2.5}$ > 20 µg m^{-3} during the 2004-2006 episodes. Finally, the air quality monitoring results from the Utö, Virolahti and Hyytiälä rural stations were used to double-check that the simultaneous high $PM_{2.5}$ peaks at Kallio and Luukki were mainly caused by LRT. During the LRT episodes, there had to be a clear $PM_{2.5}$ concentration peak at the Hyytiälä station and/or

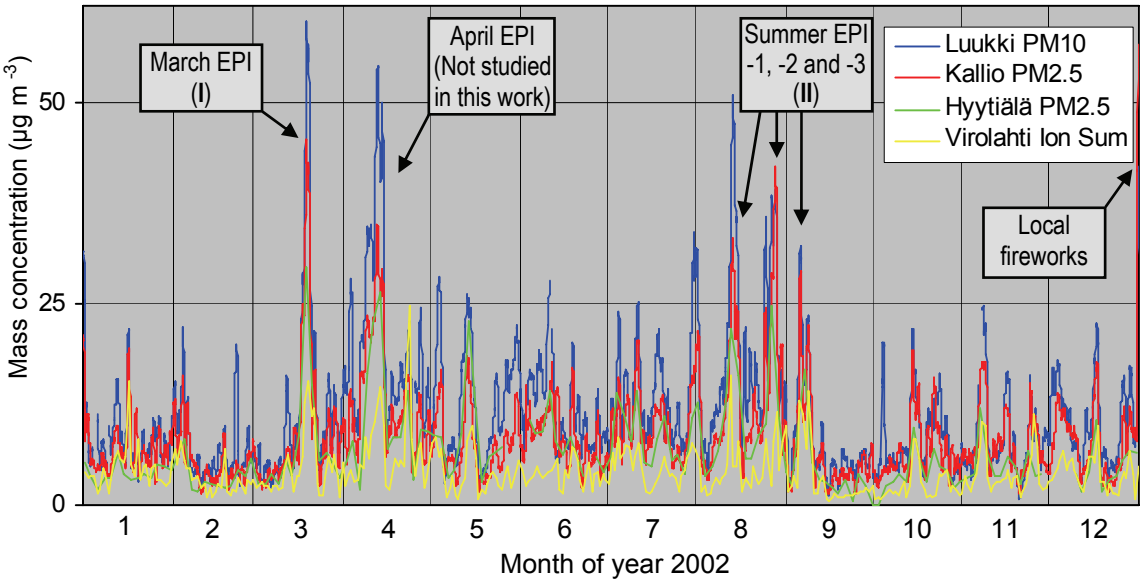

Figure 5. Air quality monitoring results from the Helsinki metropolitan area (Luukki and Kallio), Hyytiälä and Virolahti in 2002. LRT episode criteria were fulfilled during five 'EPI' periods. Luukki PM_{10} and Kallio $PM_{2.5}$ concentrations are presented as 24-h moving averages, Hyytiälä $PM_{2.5}$ shows 2-3-day averages and Virolahti ion sum (SO_4^{2-} + NO_3^- + HNO_3(g) + NH_4^+ + NH_3(g)) 24-h averages (**UP**).

ion sum peak at the Utö and/or Virolahti station. Fig. 5 shows the above-mentioned air quality monitoring results (excluding the Utö ion sum for figure clarity) for year 2002 as an example. Five periods fulfilled the above-mentioned LRT episode criteria during that year.

The 24-h moving average $PM_{2.5}$ concentrations at Kallio during 1999-2006 are shown in Fig. 6. The results (shown only for year 2002 in Fig. 5) from Luukki, Hyytiälä, Virolahti and Utö indicated that emissions from local sources caused episodic high 24-h moving average $PM_{2.5}$ peaks (> 25 μg m^{-3}) at Kallio usually only during New Year´s Eve fireworks (grey squares in Fig. 6; 24-h mean max. 63 μg m^{-3} and 1-h mean max. 193 μg m^{-3}). During the eight year period, the number of $PM_{2.5}$ LRT episodes (black dots in Fig. 6) varied between 1 and 7 per year, total number being 37. On a monthly level, the LRT episodes occurred most often in February (# 6), March (# 6), April (# 9), August (# 4) and September (# 4). During the LRT episodes, the 24-h $PM_{2.5}$ concentrations at Kallio varied between 25 and 49 μg m^{-3}, which are 3-6 times higher than the mean value (8.6 μg m^{-3}) during 1999-2006 (Fig. 6). The highest 1-h mean value was 163 μg m^{-3} during the LRT episode in August 2006.

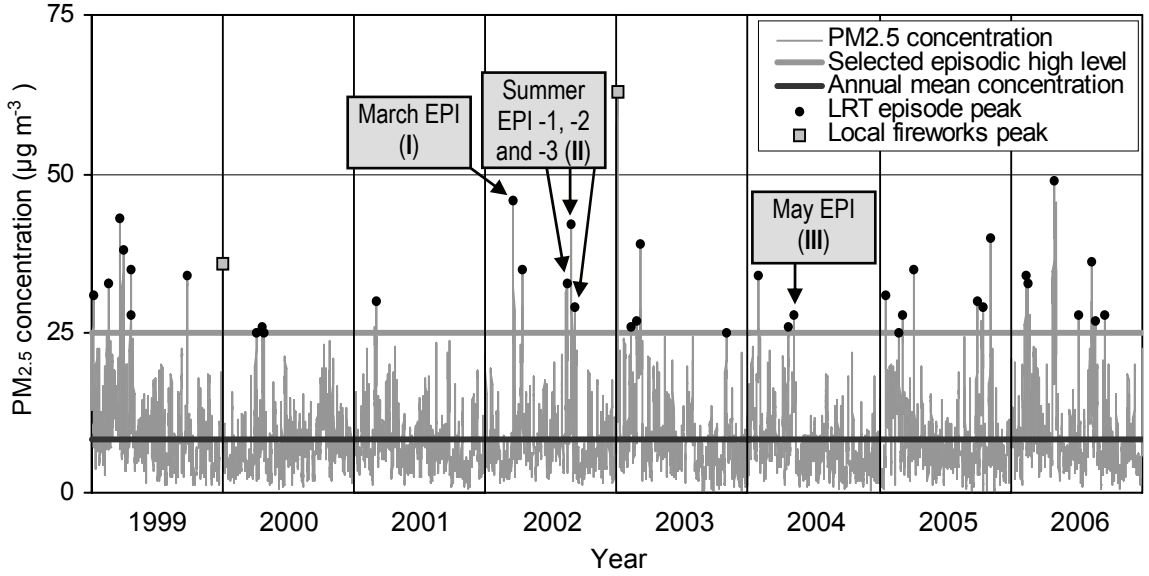

Figure 6. 24-h moving average $PM_{2.5}$ concentration at Kallio in Helsinki during 1999-2006. LRT episode peaks are depicted with black dots and the five episodes investigated in this work are shown with arrows (**UP**).

The durations of individual LRT episodes varied between 0.1 and 8.7 d. Only hours with 24-h $PM_{2.5}$ averages higher than 25 μg m^{-3} at Kallio were included in the duration, and thus weaker episode stages were excluded. The total mean duration of episodes was 0.6-15.0 d y^{-1} (average 6.0 d y^{-1}). Thus, the WHO guideline value (25 μg m^{-3}) for 24-h $PM_{2.5}$ mean concentrations was exceeded mainly due to LRT during the 1-15-d period per year in the Helsinki metropolitan area. The LRT episodes deteriorated air quality especially in 2002 and 2006, because the total durations of the episodes were quite long (total time 9.3 and 15.0 d, respectively) and the peak particle concentrations were high. The EU limit value for 24-h PM_{10} mean concentration (50 μg m^{-3}, 35 exceeded days allowed per year) was also exceeded during some LRT episodes (see PM_{10} concentrations for Luukki during year 2002 in Fig. 5 as an example). However, the clearly predominant reason for the high daily PM_{10} concentration peaks in urban areas of Finland is the resuspension of road dust particles during spring (not LRT episodes) (Anttila and Salmi, 2006).

The frequency and strength of LRT episodes of fine particles has not been determined systematically in Finland before this study. However, previous studies have also pointed out the dominant role of LRT in $PM_{2.5}$ mass concentrations in Finland and Scandinavia (Vallius et al., 2003; Karppinen et al., 2004; Forsberg et al., 2005). Even at urban traffic sites in Helsinki, 50-70% of the $PM_{2.5}$ annual mean mass concentration is caused by LRT (Vallius et al., 2003; Karppinen et al., 2004; Kauhaniemi et al., 2007). In general, the annual mean $PM_{2.5}$ concentrations are low in Finland, but during LRT episodes the daily values rise to about the same level as typically observed in the most polluted cities of Europe (Van Dingenen et al., 2004). However, even the highest daily $PM_{2.5}$ mean value (49 µg m^{-3}) of LRT episodes was clearly lower than the ordinary concentration levels of very polluted megacities, such as Beijing (annual $PM_{2.5}$ mean level ~120 µg m^{-3} in year 2000, He et al., 2001)

4.2 Characterisation of selected LRT episodes in southern Finland

Four LRT episodes of fine particles that occurred in southern Finland during year 2002 were selected for detailed characterisation and particle-source analysis (**I**, **II**). These episodes were on 17-20 March (March EPI), 12-15 August (summer EPI-1), 26-28 August (summer EPI-2) and 5-6 September, 2002 (summer EPI-3) (Figs. 5 and 6; **I**, **II**). The episodes were strongest in southern Finland, but were weaker over a large area, including as far north as Oulu, 600 km from the southern coast of Finland. The summer EPI-3 was especially intense in southeastern Finland, where the maximum hourly PM_{10} ($PM_{2.5}$ results not measured) concentrations were 200-220 µg m^{-3} (**II**). Most of the particle mass was in the $PM_{2.5}$ size range, and the $PM_{2.5}$ concentrations observed during the episodes were multifold compared with the long-term mean values. For example, the maximum 24-h moving average $PM_{2.5}$ concentrations (1-h average maxima in parentheses) at Kallio in Helsinki were 46 (58), 33 (45), 42 (54) and 29 (81) µg m^{-3} during the March EPI and summer EPI-1, EPI-2 and EPI-3, respectively (see Fig. 6).

The backward trajectories showed that air masses arrived over southern Finland from neighbouring regions of Eastern Europe during the episodes: the Baltic countries (Estonia, Latvia and Lithuania), Russia, Belarus, Ukraine and/or Poland (**I**, **II**). During the March EPI, there was an intensive agricultural field-burning period in Eastern Europe. We used data from fire-monitoring satellites to observe the largest and most intense fire areas (Fig. 7a), and air masses arrived from that direction (**I**). During the summer EPIs, satellite fire

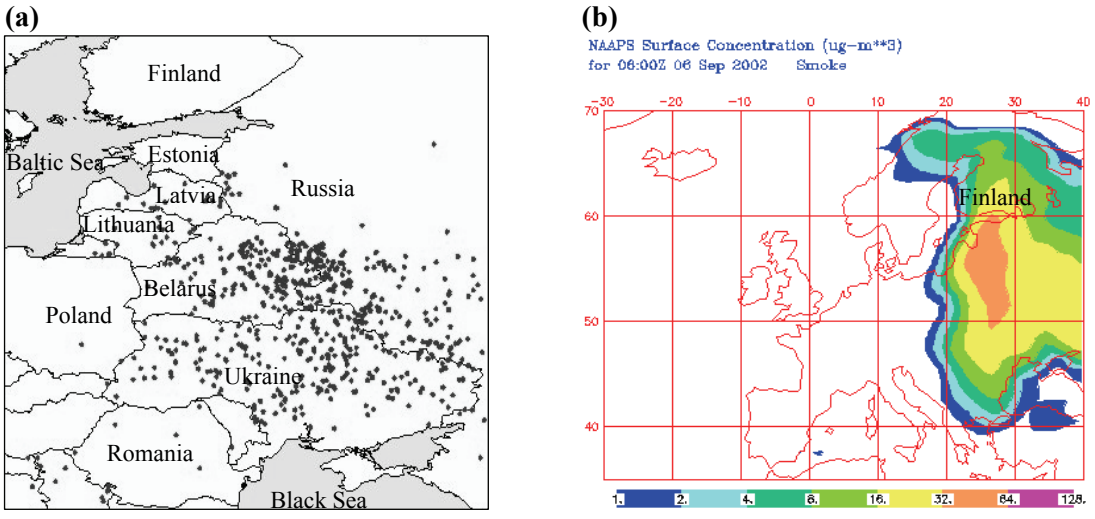

Figure 7. (a) MODIS fire detections in Eastern Europe on 16-19 March 2002 during March EPI and **(b)** NAAPS model results showing surface smoke concentrations for the strongest stage of summer EPI-3 (6 September 2002) (**I**, **II**).

detections indicated that there were numerous fire hotspots in Russia, Ukraine, Belarus and in the Baltic countries (**II**). High emissions from large forest and peat fires led to accumulation of large smoke plumes over Eastern Europe (Goldammer, 2003). The NAAPS model results indicated that the strongest smoke plumes reached Finland during the summer EPI-2 and especially during the summer EPI-3 (Fig. 7b).

4.2.1 Particle mass and number concentrations in different size fractions

The particle mass concentration in different size fractions (PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ and $PM_{>10}$) and number concentrations in the nucleation mode (3-25 nm), Aitken mode (25-90 nm) and accumulation mode (90-500 nm) were measured in Hyytiälä. The concentrations during the March EPI and summer EPIs (average of EPI-1, -2 and -3), during reference periods surrounding the episodes and during long-term reference periods (years 1999-2001 from Laakso et al., 2003) are shown in Table 3. Most of the particle mass was in the PM_1 size range during all episodes as well as on reference days. During the episodes, the particle mass increased by an average factor of 3-4 for the size classes PM_1 and $PM_{1-2.5}$ and by a factor of 2 for the size class $PM_{2.5-10}$, but above the 10-µm size class the concentration remained at about the reference level. The high mass concentration of fine ($PM_{2.5}$) particles is typical for LRT particles, due to their long residence time in the atmosphere. Furthermore, most of the particle emissions from biomass burning belong to the $PM_{2.5}$ size fraction (Andreae and Merlet, 2001; Reid et al., 2005).

Table 3. Particle mass and number concentrations in selected size fractions at Hyytiälä during March episode (March EPI; 17-20 March 2002), summer episodes (Summer EPIs; 12-15 August, 26-27 August and 6-8 September 2002) and reference days (8-28 March and 2 August – 15 September 2002, excluding episode days). Long-term (1999-2001) mean values are also shown (Laakso et al., 2003) (modified from **I** and **II**).

	PM_1 µg m^{-3}	$PM_{1-2.5}$ µg m^{-3}	$PM_{2.5-10}$ µg m^{-3}	$PM_{>10}$ µg m^{-3}	PM_{10} µg m^{-3}	Nucl. 3-25 nm # cm^{-3}	Aitken 25-90 nm # cm^{-3}	Accum. 90-500 nm # cm^{-3}	Total 3-500 nm # cm^{-3}	Accum. to Aitken ratio
March EPI	15.4	6.9	2.3	0.3	24.6	273 *211	955	2703	3924 *3867	2.83
March references	3.6	1.2	1.1	0.3	5.9	1713 *1161	1525	480	3717 *3166	0.31
Spring mean Laakso et al. (2003)	4.4	2.0	1.0	-	7.4	- *810	1270	660	- *2720	0.52
Summer EPIs	15.9	3.7	2.3	0.7	21.9	226 *174	588	1067	1880 *1828	1.81
Summer references	5.3	1.2	1.2	0.6	7.7	489 *343	1138	591	2219 *2072	0.52
Summer-autumn mean Laakso et al. (2003)	4.6	1.2	1.3	-	7.1	- *365	1065	710	- *2130	0.67

* Denotes the concentration calculated with nucleation mode limits 10-25 nm as in Laakso et al. (2003).

The particle number concentration increased by a factor of 2-5 in the accumulation mode and decreased in the Aitken (factor of 0.5-0.8) and nucleation modes (factor of 0.2-0.5) (Table 3; **I**, **II**). The decrease in the smallest particles was expected, since small molecular clusters and particles are scavenged efficiently by a large number of bigger particles (e.g. Mönkkönen et al., 2004; Stohl et al., 2007b). Furthermore, the abundant surface area of accumulation mode particles consumes condensable vapours, preventing particle formation and growth. The total concentration of particles with a diameter less

than 500 nm was moderately unaffected, since the decrease in nucleation and Aitken mode concentrations was balanced by the increase in accumulation mode concentrations.

Aitken mode concentrations normally exceed those of the accumulation mode in Hyytiälä (accum./Aitken ratio values ~ 0.3-0.7 during reference and long-term periods, Table 3), and high values of accum./Aitken ratios are typical for polluted air masses transported over long distances (mean values during the March EPI and summer EPIs were 1.8 and 2.8, respectively, Table 3), since the sources for accumulation mode particles are scarce in the area around Hyytiälä and Aitken mode particles have shorter lifetimes than accumulation mode particles. Aitken mode particles cannot be transported in the atmosphere from as far away as accumulation mode particles because the deposition efficiency of Aitken mode particles is high, they disappear by colliding and sticking to the accumulation mode particles and they grow rapidly due to condensation of vapours and to cloud processes (Seinfeld and Pandis, 1998). Therefore, the high values of accum./Aitken ratios may thus be an indicator for LRT episodes in general. For instance, Aarnio et al. (2007) successfully used accum./Aitken ratios as indicators to distinguish local PM_{10} episodes from LRT episodes in the Helsinki metropolitan area.

4.2.2 Chemical composition and major sources of particles

The chemical composition of particles during the episodes was investigated to identify the main origins of the particles. Here (**I**, **II**), the SO_4^{2-}, total nitrate and total ammonium monitoring results from Virolahti, Utö and Ähtäri were utilized. Furthermore, daily samples from particle mass monitors in the Helsinki metropolitan area and in Imatra (only during summer EPI-3) were analysed with SEM/EDX.

The 24-h mean TSP concentrations of SO_4^{2-}, total nitrate and total ammonium increased strongly at Virolahti, Utö and Ähtäri during the episodes (**I**, **II**). For instance, the mean ion sum (total amount) of the concentrations of these chemical components at Virolahti were 13.1, 8.2, 7.2 and 12.1 μg m^{-3} during the March EPI and summer EPI-1, EPI-2 and EPI-3, respectively (daily values shown in Fig. 5). The ion sum in Utö was similar to that in Virolahti, whereas that in Ähtäri, a more northerly station, was clearly lower (factor of ~ 2/3). The values during the episodes were 3-5 times higher than those usually observed at these three stations at those times of the year (Leinonen, 2001).

The ion sum and PM_{10} concentration were compared in Virolahti during the summer EPIs and reference period (**II**). A similar comparison could not be performed for the March EPI because PM_{10} monitoring was not yet initiated at Virolahti during that time. The ion sum/PM_{10} ratios were lower than usual during the episodes; the means were 0.28, 0.18, 0.17 and 0.33 during the summer EPI-1, EPI-2, EPI-3 and reference period, respectively. This indicates that the PM contained unusually high fractions of chemical components other than SO_4^{2-}, NO_3^- and NH_4^+ during the summer EPIs. The ion sum/ PM_{10} ratio was especially low (0.14) during the peak stage of EPI-3 (September 6, 2002), when the strongest smoke plume from wildfires reached southeastern Finland. Large emissions of OC and EC and other chemical components from wildfires were probably the main reasons for the reduction in relative fraction of the ion sum during the episodes.

The elemental composition of single particles and agglomerates was analysed with the SEM/EDX method from samples collected during the episodes and the reference days. The $PM_{2.5}$ samples from Helsinki were selected during the March EPI and summer EPI-1

and EPI-2. The EPI-3 was clearly strongest in southeastern Finland, but unfortunately no $PM_{2.5}$ samples were collected during that time there. Therefore, the PM_{10} samples from Imatra were studied during EPI-3. The particles were classified into six different groups based on the most abundant elements in each particle or agglomerate: (1) S, (2) Si or Al, (3) Ca, (4) Fe, (5) Na or Cl and (6) low-Z. Particles and agglomerates in the low-Z class contained only elements with an atomic number lower than 11 (Na), such as C, N and O, which could not be analysed quantitatively with the SEM/EDX used. SEM/EDX analysis of particle and agglomerates showed that the proportion of S-rich particles and agglomerates was extraordinarily high during the episodes, compared with the reference periods (Fig. 8). The $PM_{2.5}$ samples of the urban background station at Kallio contained abundant S-rich particles (~60-90%) during the March EPI and summer EPI-1 and EPI-2, but only an average of 10% (range 7-13%) during the reference days. The fraction of S-rich particles was also high (55%) during the peak day of EPI-3 in Imatra compared with the value (3%) of the reference day. Most of the individual S-rich particles were small (geometric diameter < 1 μm), but they usually formed larger agglomerates (geometric diameter > 1 μm) that could be analysed with the SEM/EDX device used. A substantial part of the agglomeration probably occurred during particle sampling and sample preparation for the SEM/EDX analyses.

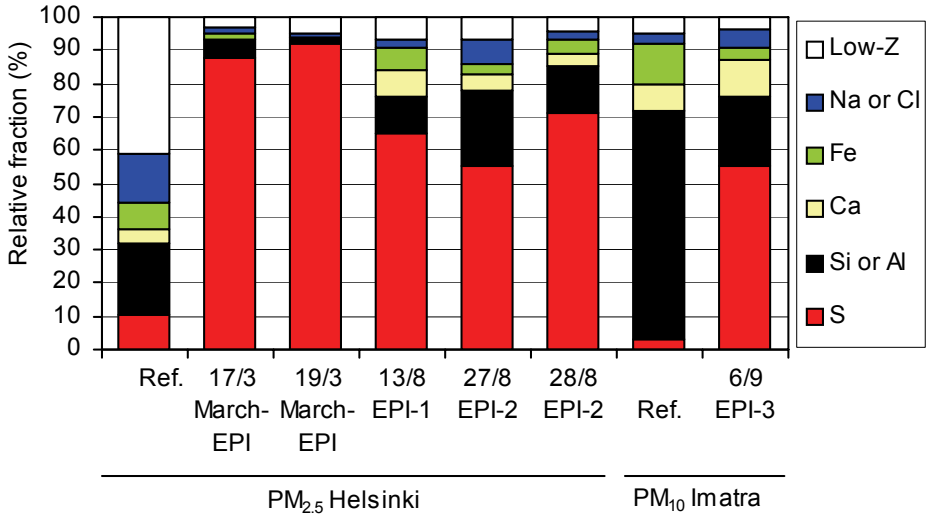

Figure 8. Abundance of particle groups (%) in reference samples and episode samples collected at Kallio station in Helsinki during March EPI (17 and 19 March 2002), summer EPI-1 (13 August 2002) and summer EPI-2 (27 and 28 August 2002) and at Mansikkala station in Imatra during summer EPI-3 (6 September 2002) (modified from **I** and **II**).

In addition to S, S-rich particles and agglomerates contained large amounts of C and O as well as some Na, Si and K (EDX spectra shown in **I** and **II**). One of the main chemical components in S-rich particles and agglomerates was doubtless SO_4^{2-}. High increase in SO_4^{2-} (as well as in NO_3^- and NH_4^+) concentrations during the episode were already confirmed by ion concentration results, as was mentioned above. However, the SEM/EDX analyses showed that there was an unusually high proportion of K in S-rich particles during the episodes. The relative weight percentages (sum of all analysed elements normalized to 100%) of K in S-rich particles were higher during all episodes (11.4-19.3% for the March EPI, 8.9% for summer EPI-1, 8.9% for EPI-2 and 8.2% for EPI-3) than in the reference days (6.3%) (**I**, **II**). These differences were statistically significant ($p < 0.01$, Mann-Whitney U-test). The median S/K ratios of S-rich particles

showed the same change; the S/K ratios were lower during the March EPI (2.1-5.2), EPI-1 (5.5), EPI-2 (5.4) and EPI-3 (6.0) than during the reference days (7.8). The increased fraction of K is an indication of emissions from biomass burning (Andreae, 1983, 1998). The trajectories, fire area maps and NAAPS model results indicate that during the episodes the major part of the biomass-burning emissions originated from large-scale open biomass burning in Eastern Europe. Part of the biomass-burning emissions may also have originated from other biomass-burning sources (e.g. wood combustion) in these areas (Liousse et al., 1996; Bond et al., 2004).

The relative weight percentages of K in S-rich particles did not rise during the summer EPIs (range 8.2-8.9%) as high as during the March EPI (range 11.4-19.3%). The smouldering burning conditions are more predominant in boreal forest fires and peat fires than in grass, shrub or cereal waste fires, which mainly burn under flaming conditions (Echalar et al., 1995; Lavoué et al., 2000; Ortiz de Zárate et al., 2000; Soja et al., 2004). Thus the aerosols from forest and peat fires were apparently less enriched in K than aerosols from agricultural field burning, since the fraction of K is lower in emissions from smouldering fires compared with flaming fires (Echalar et al., 1995; Gaudichet et al., 1995; Robinson et al., 2004). Another reason that has doubtless decreased the relative proportion of K in all episode samples is the mixing of S-rich emissions from fossil fuel burning, since air masses arrived from the regions of Eastern Europe with high S emissions (EMEP, 2001).

The PM measurements performed in Helsinki and Hyytiälä showed that the mass concentrations of coarse ($PM_{2.5-10}$) particles also increased slightly during the episodes (previous section; **I**, **II**). The composition of coarse particles from the PM_{10} samples was studied with the SEM/EDX method during the summer EPIs. The individual particle results showed that the relative proportion of different Ca-rich particle types increased during the episodes (**II**). Typical elements included Ca, Ca-S-(Si-Na), Ca-(S-Si-Al) and Ca-Mg-(Si) (minor elements in parentheses), which suggests that major components of Ca-rich particles could have been different Ca and Ca/Mg carbonates, sulphates and/or nitrates. Their mode and median sizes (geometric diameter) were 2 and 3 μm, respectively. Forest and peat fires were probably some of the major sources of Ca-rich particles, since these particles are emitted from incomplete burning of biomass and most of their mass is in the coarse (D_p > 1 μm) size fraction (Allen and Miguel, 1995; Osan et al., 2002; Li et al., 2003b; Pagels et al., 2003). However, they may also have originated from large emissions of Ca-rich particles from the Estonian and Russian oil-shale-burning industrial areas located in Narva (location shown in Fig. 3) and Slantsy (~25 km south from Narva) during the summer EPI-1 and EPI-2, since the trajectories passed over that region (**II**).

A detailed bulk chemical characterisation of size-segregated aerosols during the summer EPI-2 and EPI-3 in Helsinki is presented in Sillanpää et al. (2005) because their field campaign (23 August - 23 September, 2002) was conducted during the episodes. During both episodes, the ∑MA and K^+ concentrations increased strongly in the $PM_{2.5}$ size fraction (Sillanpää et al., 2005), indicating that biomass burning was a major source of aerosols. The elevated Ca concentrations were also observed in the coarse thorasic ($PM_{2.5-10}$) size fraction by Sillanpää et al. (2005). The inorganic secondary aerosols (NO_3^-, SO_4^{2-}, NH_4^+) and several metals (e.g. Pb, V and Ni) attained their highest concentration during EPI-3, representing emissions from fossil fuel combustion and industrial sources (Sillanpää et al., 2005). However, the results of EPI-3 can not be compared favourably here (**II**) because the $PM_{2.5}$ samples were collected in Helsinki

(not in Imatra) and the sampling time for that period was very long (5-9 September 2002, 97 h) in Sillanpää et al. (2005). At the end of their sampling period, the trajectories arrived from clearly different, more westerly regions compared with the peak stage of the EPI-3. In conclusion, daily $PM_{2.5}$ samples from routine mass-monitoring measurements are not ideal for detailed individual particle analysis with the SEM/EDX method, due to agglomeration of particles during sampling and sample preparation, although they can be utilized successfully to identify *major* changes in elemental composition and emission sources of particles during different episodes. Further detailed chemical characterisation of aerosols during intensive field campaigns can provide a more elaborate view on particle composition and sources (**III**).

4.2.3 Discussion of LRT episode sources

Several LRT episodes of fine particles usually occur every year in southern Finland, as was described in section 4.1. In this thesis, particle source identification is presented for four LRT episodes in 2002 (previous section; **I**, **II**) and during a single episode on 5-9 May, 2004 (May EPI in Fig. 6; **III**). During the May EPI, the aerosols originated mainly from polluted areas of Eastern Europe, and some smoke from open biomass burning was also brought in by LRT. Since the main focus (**III**) was to investigate detailed individual particle composition of aerosols during polluted and unpolluted LRT periods, the results of the May EPI are presented in the next section and discussion of the LRT episode source regions and emission source types is presented here.

During the five LRT episodes studied in this thesis, the aerosols originated mainly from the following regions of Eastern Europe: Estonia, Latvia, Lithuania, Russia, Belarus, Ukraine and/or Poland. Niemi et al. (2006a, b) studied the potential source areas of aerosols during all the LRT episodes in 1999-2006 (# 37, shown in Fig. 6), and practically all 96-h backward air mass trajectories originated over the above-mentioned countries. Sogacheva et al. (2005) also showed that high accumulation mode number concentrations in Hyytiälä are observed when air masses arrive from Eastern Europe. In conclusion, the highest LRT episode peaks in southern Finland are caused by emissions from Eastern Europe. However, it is important to note that the predominant wind direction in Finland is from the southwest and, therefore, a significant proportion of LRT aerosols originate from more westerly source regions (and from other directions) when the concentrations of fine particles are below the episodic level.

The emission sources of aerosols during LRT episodes have been studied in detail during few episodes in Finland, in addition to the March EPI (**I**), summer EPIs (**II**) and May EPI (**III**). On 19-20 February 1998, an LRT episode peak was caused by sea salt from the Atlantic Ocean and by anthropogenic emissions from Western Europe (Tervahattu et al., 2002a, b). A very unusual episode was observed in Finland on 16-22 September 2001; the particles were mainly in the coarse size fraction ($PM_{2.5-10}$; the $PM_{2.5}$ peak is also clear in Fig. 6 but it did not exceed the 25 μg m^{-3} level) and their main source was fly ash emissions from Estonian and Russian oil-shale-burning industrial origins in Narva and Slantsy with minor amounts of soil dust from the Kazakhstan Ryn Peski Desert (Hongisto and Sofiev, 2004; Tervahattu et al., 2004). During year 2006, emissions from open biomass-burning fires in Eastern Europe caused strong LRT episodes of fine particles several times (25 April - 6 May, 7-15 August and 21 August 2006) in large areas over Finland (Niemi et al., 2006b; Saarikoski et al., 2006, 2007). The spring episode (25 April - 6 May 2006) was mainly caused by both intensive agricultural field burning and wildfires in Eastern Europe, and very high

particle concentrations were even observed in Svalbard and in the United Kingdom (Stohl et al., 2007a; Witham and Manning, 2007).

A long-term characterisation of aerosol sources during LRT episodes of fine particles in 2001-2005 in southern Finland was presented by Niemi et al. (2006a, b; see LRT episode peaks in Fig. 6). The proportions of aerosols from open biomass burning were estimated during the episodes based on daily MODIS fire hotspot detections, backward air mass trajectories, NAAPS smoke dispersion modelling results and chemical analysis of particles. Half of the episodes were at least partly caused by emissions from open biomass burning, while the other half were mainly caused by the LRT of ordinary anthropogenic pollutants (from energy production, traffic, industry, residential burning etc.) originating from Eastern Europe. However, the highest particle concentrations and longest episode periods were caused by emissions from open biomass burning (Niemi et al., 2006a, b).

In conclusion, smoke from open biomass burning is an important factor in the deterioration of air quality locally and occasionally even regionally in the eastern parts of Europe, especially during warm and dry periods in spring and late summer. Sometimes these fires cause high particle concentrations even at distances from hundreds to thousand(s) of kilometres from the fire areas. The inventories for open biomass-burning emissions are quite inaccurate, mainly due to difficulties in estimating the amount of biomass burned (Andreae and Merlet, 2001; Bond et al., 2004; van der Werf et al., 2006; Niemi, 2007; van Aardenne et al., 2007). Therefore, it is also difficult to compare emissions rates of open biomass burning to those of other anthropogenic emission sources. However, it is clear that the emissions from open biomass burning form a substantial proportion of the total anthropogenic emissions in southern and eastern regions of Europe (Andreae and Merlet, 2001; Bond et al., 2004; van der Werf et al., 2006; EMEP, 2006a; Niemi, 2007; van Aardenne et al., 2007). Their total impact on air quality in Finland and in other parts of Europe has not yet been estimated properly.

4.3 Comparison of polluted and unpolluted LRT periods in southern Finland

The chemical composition, morphology, mixing state and sources of individual aerosol particles were studied in three size fractions ($PM_{0.2\text{-}1}$, $PM_{1\text{-}3.3}$ and $PM_{3.3\text{-}11}$) with the TEM/EDX method from samples collected at the Hyytiälä rural station during a field campaign in May 2004 (**III**). In addition, the TEM/EDX results were complemented with the size-segregated bulk chemical measurements of selected ions, OC and EC. The particle samples for TEM/EDX analysis were collected during an LRT pollution episode (PM_1 ~16 μg m^{-3}), an intermediate period (PM_1 ~5 μg m^{-3}) and clean periods (PM_1 ~2 μg m^{-3}) (Fig 9a). The air mass backward trajectories showed that during the pollution episode the continental air masses arrived from the direction of southwestern Russia, Belarus and Ukraine (Fig. 9b), which belong to typical source regions for the LRT episodes observed in Finland (Sogacheva et al., 2005; Niemi et al., 2006a). During the intermediate period, the backtrajectories originated from the northeast and curved towards the Arctic Ocean. During the clean period air masses arrived in Finland from the Arctic Ocean, passing over Norway and Sweden, which is a typical source sector for very low particle mass concentrations (Sogacheva et al., 2005) due to minor anthropogenic emissions.

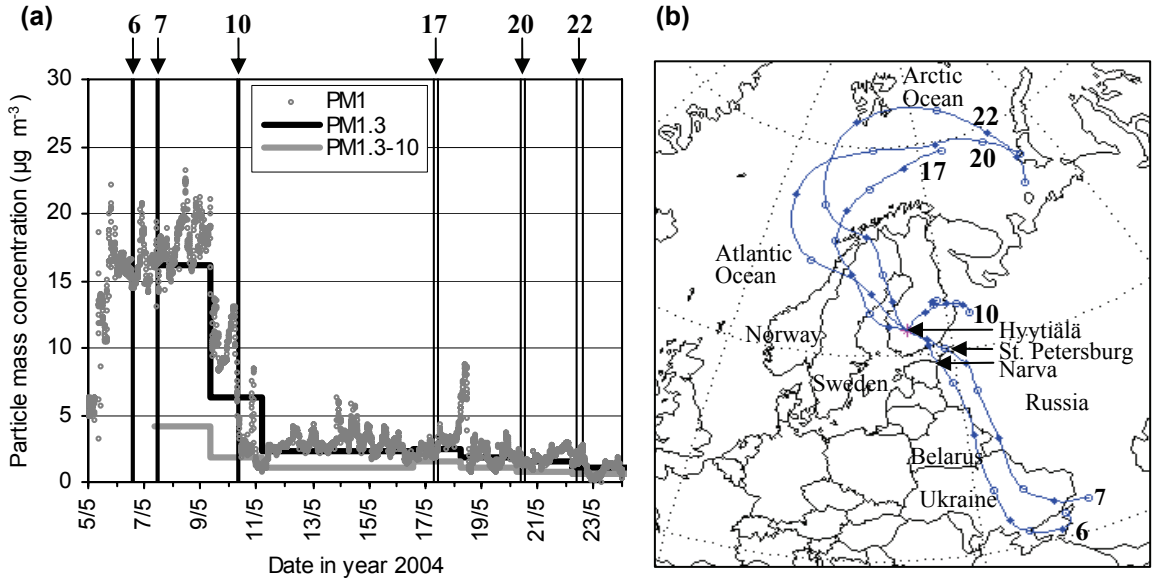

Figure 9. (a) Particle mass concentrations (PM_1 measured with ELPI, and $PM_{1.3}$ and $PM_{1.3\text{-}10}$ with VI) in Hyytiälä in May 2004. The six sampling periods with the Battelle impactor for TEM/EDX analysis are marked with vertical lines and arrows (sample numbers above). **(b)** Backward air mass trajectories arriving at 250-m level in Hyytiälä during the six sampling periods in May 2004. Date numbers (= sample numbers) of each trajectory are shown, and symbols represent 12-h intervals (total time 96 h) (**III**).

Bulk chemical results showed that the following chemical components attained their maximum concentrations during the pollution episode: OC, EC, SO_4^{2-}, NH_4^+, NO_3^-, Ca_2^+, K^+, Mg^{2+}, oxalate, malonate, succinate and ∑MA (**III**). During the clean period, the concentrations of Na^+, Cl^- and MSA were elevated, which confirms the marine origin of the air mass. The concentrations of most chemical components during all periods were much higher in the $PM_{1.3}$ samples than in the $PM_{1.3\text{-}10}$ samples. The main components in all $PM_{1.3}$ samples were OC, SO_4^{2-}, NH_4^+ and EC, their total proportions in the $PM_{1.3}$ mass being 73-83%. However, NO_3^-, Cl^-, Na^+ (not during the pollution episode), Mg^{2+} and Ca^{2+} were mostly present in the coarse ($PM_{1.3\text{-}10}$) size fraction.

4.3.1 Individual particle types and their sources

The individual particles analysed were classified into 10 different particle groups based on their elemental composition, morphology, internal structure and susceptibility to damage by an electron beam. The particle groups and classification criteria are presented in Table 4. The relative abundances of each particle group in different size fractions are shown in Table 5. The particles of the first three groups were mostly present in the $PM_{0.2\text{-}1}$ samples. These particle types were 1) tar balls, 2) soot and 3) (ammonium)sulphates and their mixtures with C, K and/or different inclusions. The relative proportions of the remaining seven particle groups were usually highest in either in the $PM_{1\text{-}3.3}$ or $PM_{3.3\text{-}11}$ samples: 4) silicates, 5) metal oxides/hydroxides, 6) Ca/Mg carbonates, sulphates and/or nitrates, 7) sea salt, 8) porous Na-rich particles, 9) biological particles and 10) C-rich fragments. The description of the particle types, their sources, and changes in their relative abundances related to aerosol source areas are summarized below.

Table 4. Classification criteria for different particle groups (**III**).

Particle group	Elemental characteristics *	Typical morphology/internal structure and beam sensitivity
Tar balls	Abundant C with minor S, often minor K	Individual particles with circular shape
Soot	Abundant C, often minor S, K and/or Si	Fractal-like agglomerates of circular particles
(Ammonium)sulphates and their mixtures with C, K and/or different inclusions	S with variable amounts of C and/or (usually minor) K	Mostly circular shape, beam damage, sometimes contains internally mixed soot and other beam-resistant inclusions
Silicates	Abundant Si, usually with Al, variable minor Fe, Ca, K, Mg, Na, Ti and/or S	Irregular soil particles or circular fly ash particles
Metal oxides/hydroxides	Abundant Mn, Fe, Zn and/or Pb	Irregular angular particles or circular fly ash particles
Ca/Mg carbonates, sulphates and/or nitrates	Abundant Ca with C and/or S, sometimes with abundant Mg and/or minor Si	Mostly circular shape, sometimes angular
Sea salt	Abundant Na, variable Cl, S, Mg, K, Ca	Variable morphology; different angular shapes or circular
Porous Na-rich particles	Abundant Na with S and K, no Mg and Ca	Spongelike porous morphology
Biological particles	Abundant C, usually minor K and/or P	Variable morphology
C-rich fragments	Abundant C	Angular shape, often thin

* Oxygen was present in practically all particles and therefore is not shown in the element lists.

Table 5. Relative abundances (%) of particles in different particle groups in three size fractions during the six sampling periods in May 2004 (**III**).*

Size fraction	0.2 µm < Dp < 1 µm						1 µm < Dp < 3.3 µm						3.3 µm < Dp < 11 µm					
	Pollution episode		Int. per.	Clean marine period			Pollution episode		Int. per.	Clean marine period			Pollution episode		Int. per.	Clean marine period		
Sample number (= date)	6	7	10	17	20	22	6	7	10	17	20	22	6	7	10	17	20	22
Tar balls	1	2	0	0	0	0	**4**	**4**	2	0	0	0	0	0	0	0	0	0
Soot	7	3	**12**	0	3	6	0	0	2	0	0	0	11	5	0	0	0	0
(Ammonium)sulphates and their mixtures with C, K and/or different inclusions	84	87	83	95	**97**	93	9	14	5	6	2	15	0	0	0	5	0	0
Silicates	4(1)	4(2)	0	3	0	0	22(1)	26(7)	14(2)	17	2	5	32	33	0	**53**	5	6
Metal oxides/hydroxides	1	4(2)	0	1	0	1	4(1)	9(1)	0	0	0	3(1)	5	5(5)	**11**(6)	0	0	3
Ca/Mg carbonates, sulphates and/or nitrates	1(1)	0	0	0	0	0	**48**(22)	39(27)	3(3)	10(6)	2(2)	1(1)	26(21)	38(29)	6(6)	0	5(5)	0
Sea salt	1	0	3	1	0	0	9	4	36	67	**89**	73	5	0	5	21	25	0
Porous Na-rich particles	0	0	0	0	0	0	0	0	**35**	0	0	0	0	0	5	0	0	0
Biological particles	0	0	0	0	0	0	0	0	2	0	2	0	21	14	50	0	55	**81**
C-rich fragments	1	1	2	0	0	1	5	4	2	0	5	3	0	5	**22**	21	10	10
Number of analysed particles (n)	136	103	104	100	102	103	85	74	63	63	64	73	19	21	18	19	20	31

* Maximum value of each particle group is shown with bold numbers. Int. per. = Intermediate period. The values in parentheses show the abundances of spherical/rounded particles.

Tar balls. During the pollution episode, the $PM_{0.2\text{-}1}$ and $PM_{1\text{-}3.3}$ samples contained some (1-4%; Table 5) individual spherical C-rich particles that were very dark (electron-dense), amorphous and totally stable even in the presence of a very strong electron beam (Fig. 10, particle A). Pósfai et al. (2003; 2004) named these particles tar balls, a carbonaceous particle type distinct from soot. Tar balls originate from biomass burning,

especially during smouldering burning conditions, and they contain abundant OC (Pósfai et al., 2003, 2004; Hand et al., 2005; Chakrabarty et al., 2006). The relative proportion of the tar balls remained quite low or moderate (1-4%) during the pollution episode compared with the proportions observed at some other sites (Pósfai et al., 2003, 2004; Hand et al., 2005). The low proportion of tar balls was consistent with bulk chemical results showing that the concentrations of chemical tracers (K^+ and ∑MA) for biomass-burning aerosols increased clearly during the episode, although the ∑MA concentration remained quite low compared with the values observed during strong LRT episodes in Finland that originated from open biomass-burning fires (Sillanpää et al., 2005; Saarikoski et al., 2007). Thus, biomass burning was one source but not the main source of the LRT pollution episode. The major source for biomass-burning aerosols could be fires in Eastern Europe, especially in Russia, based on MODIS fire detections and NAAPS smoke dispersion modelling results (**III**).

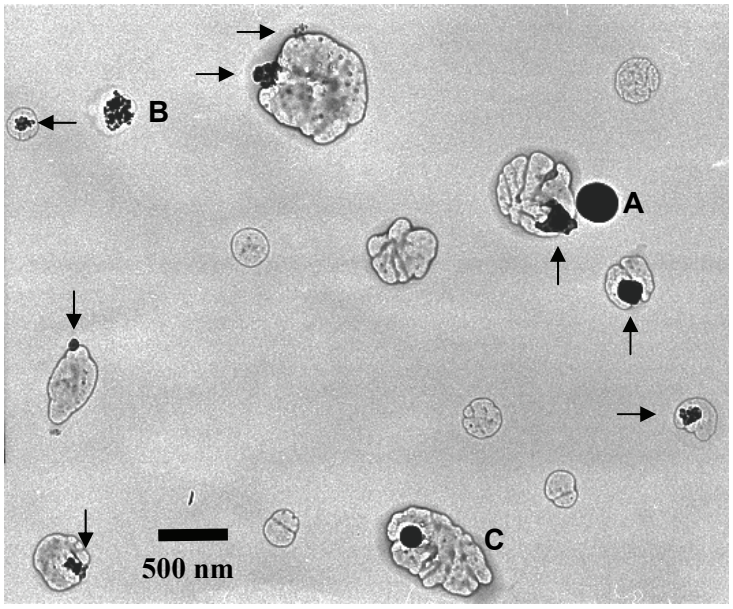

Figure 10. TEM images of different particle types from $PM_{0.2\text{-}1}$ sample 7 collected during the pollution episode; **(A)** tar ball, **(B)** soot and **(C)** Si-rich fly ash mixed with (ammonium)sulphate-containing material. The remaining particles were classified as '(ammonium)sulphates and their mixtures with C, K, soot (depicted with horizontal arrows) and/or with other inclusions (depicted with vertical arrows)' (**III**).

Soot. Soot particles (Fig. 10, particle B; **III**) were present in almost all $PM_{0.2\text{-}1}$ samples (0-12%) and they originated from various burning sources. Several soot particles were strongly mixed with beam-sensitive, S-containing material, and they were included in the particle group described in the next paragraph (these mixed soot particles were not included in the above-mentioned percentage value).

(Ammonium)sulphates and their mixtures with C, K and/or different inclusions. Most particles (83-97%) in the $PM_{0.2\text{-}1}$ samples were easily damaged under beam exposure. These particles contained S with variable amounts of C, O and (usually minor) K. Sometimes minor amounts of other elements (Mg, Ca, Na, Si and Al; during the pollution episode also Pb, Zn, V and Ni) were also detected. The S in these particles was probably present mainly as ammonium sulphate salts (e.g. $(NH_4)_2SO_4$, $(NH_4)HSO_4$), $(NH_4)_3H(SO_4)_2$) because the particles did not have satellite droplet ring(s)

around them, which is characteristic of such acid sulphates as H_2SO_4 particles (Pósfai and Molnár, 2000; Kojima et al., 2004, 2005). The high concentrations of SO_4^{2-} and NH_4^+ measured with a bulk chemical method (IC) also support the predominance of ammonium sulphate salts. Since NH_4^+ (and NO_3^-) cannot be detected with EDX, we decided to name the S-containing components of these particles as (ammonium)sulphates. Furthermore, some of these beam-sensitive particles contained abundant C (and only minor S), beam-resistant soot agglomerates (2-22% of all particles in the PM_1 sample) and some particles also contained other beam-resistant dark (= electron-opaque) inclusions without clear morphological characteristics (Fig. 10; **III**). In Europe, SO_4^{2-} originates mostly from fossil fuel burning, NH_4^+ from agriculture and carbonaceous material from fossil fuel and biomass burning as well as from biogenic emissions (Bond et al., 2004; Schaap et al., 2004; Kanakidou et al., 2005; EMEP, 2006a, b; WHO, 2006b; Kupiainen and Klimont, 2007; van Aardenne et al., 2007).

Silicates and metal oxides/hydroxides. The shape of silicates and metal oxides/hydroxides was usually angular, but a few spherical fly ash particles were also observed (Fig. 10, particle C). The proportions of both angular and spherical silicates and metal oxides/hydroxides were especially high during the pollution episode (Table 5), and Pb-containing particles were observed only during this period. When all particles with at least minor (detectable) levels of Pb were counted from all particle groups (some S-C-K-rich particles also contained Pb as mentioned above), the proportions of Pb-containing particles were 3-7% in the $PM_{1\text{-}3.3}$ and $PM_{0.2\text{-}1}$ samples. These elevated proportions of heavy metals and fly ash particles indicate that polluted air masses from Eastern Europe carried aerosols from the metal industry and/or fossil fuel burning (Vestreng et al., 2006; Murphy et al., 2007). During the pollution episode, the proportions of metal oxide/hydroxide particles were quite similar to or lower than their proportions at rural sites in central and northeastern Germany during the field campaigns in 1998-1999 (~1-20%, Ebert et al., 2002, 2004).

Ca/Mg carbonates, sulphates and/or nitrates. Ca-O-rich particles with variable levels of Mg, C, S and Si were classified as Ca-rich particles, and this group was named 'Ca/Mg carbonates, sulphates and/or nitrates' based on the elemental ratios in the particles (**III**). The relative number proportion of these Ca-rich particles was very high during the pollution episode, especially in the $PM_{1\text{-}3.3}$ samples (39-48%) but also in the $PM_{3.3\text{-}11}$ samples (26-28%). During this time, air masses passed over the Estonian and Russian oil-shale-burning industrial areas located in Narva and Slantsy and over the region of St. Petersburg. These regions belong to the strongest source areas of aerosols and Ca in Northern Europe (Häsänen et al., 1997; Lee and Pacyna, 1999; Jalkanen et al., 2000; EMEP, 2002), and therefore Ca-rich particles in the pollution episode may have originated mainly from these areas. However, detailed source identification of Ca-rich particles is difficult because they can originate from various sources, including fossil fuel and biomass burning, the cement and metal industries, soil dust and marine sources (Hoornaert et al., 1996; Lee and Pacyna, 1999; Li et al., 2003b).

Sea salt. The relative proportions of SSPs rose especially high in the $PM_{1\text{-}3.3}$ size fraction (67-89%) during the clean period, when air masses arrived from the direction of the Arctic Ocean. The rate of Cl^- depletion from sea salt varied markedly, depending on the time spent over the continent (**III**).

Porous Na-rich particles. During the intermediate period, the $PM_{1\text{-}3.3}$ sample contained ordinary SSPs (36%) and also other Na-rich particles (35%) without the characteristic morphology and Mg-Ca-K ratios of sea salt. The morphology of the Na-rich particles

was rounded and porous (spongelike), and they were apparently composed of numerous, small spherical subparticles (Fig. 11a, particles no. 2, and Fig. 11b). These porous particles contained abundant Na and O and some S and K, while Mg and Ca were (almost) totally absent (compare spectra in Fig. 11c and d). During their sampling, the air masses had passed over paper industry areas located ~100 km northeast of Hyytiälä. Large amounts of sodium sulphate (Na_2SO_4) are used in wood pulp processing, and residuals from these processes are burned. Thus, the burning of mixed Na_2SO_4 and biomass residuals (contain abundant K) could be the source of the Na-S-K-O-rich particles. However, burning of other waste is also a potential source for these particles (Hwang and Ro, 2006a), because waste burning is a major source of Na in continental areas (Ooki et al., 2002).

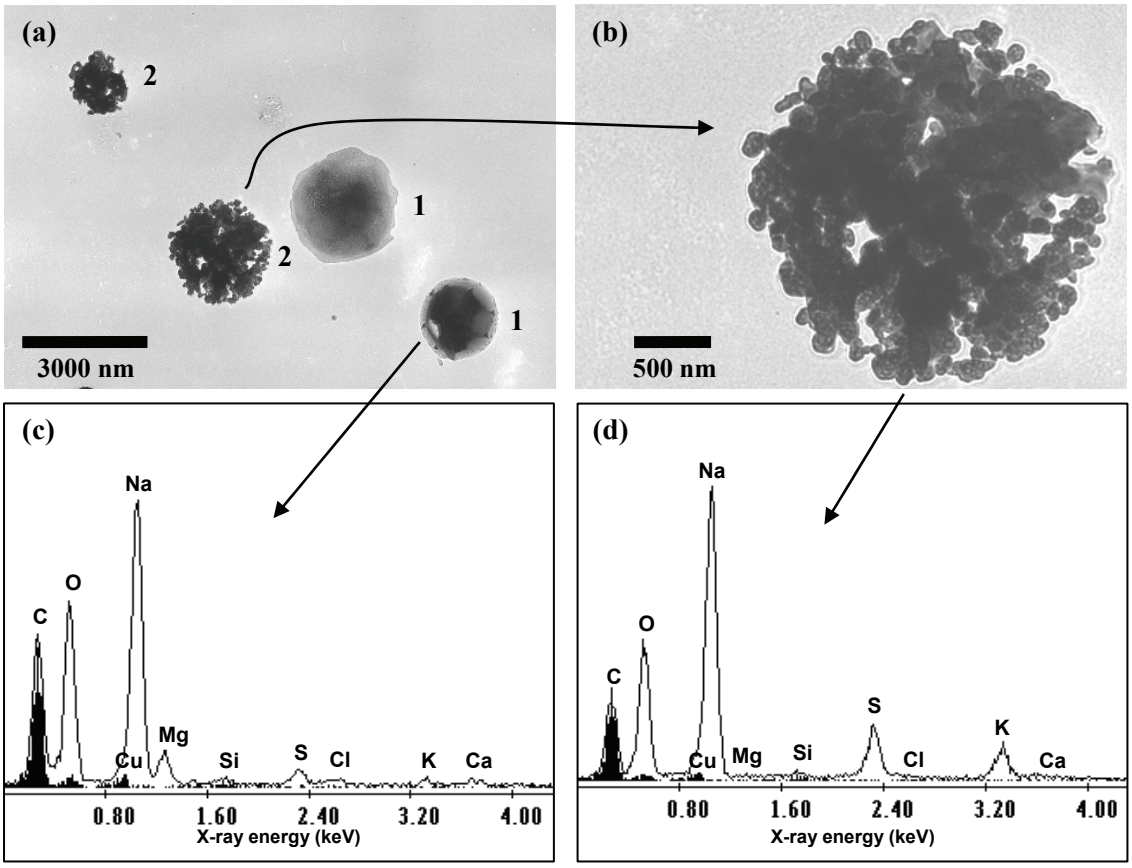

Figure 11. TEM images of **(a1)** sea-salt particles with strong Cl^- depletion and **(a2 and b)** porous Na-S-K-O-rich particles. The X-ray spectra **(c and d)** show that porous particles did not contain Mg and Ca and that the proportion of K was high compared with elemental ratios in sea salt (background spectra from TEM grid substrate are depicted with black colour) (**III**).

Biological particles and C-rich fragments. The morphology of biological particles varied strongly from spherical and oval to complicated biological structures (**III**). There were also several angular C-rich particles without the clearly characteristic morphology of biological particles, and due to uncertainty in source identification, they were referred to as C-rich fragments. These C-rich fragments contained no P or K, which are typical minor elements in biological particles. However, the thin and angular appearance of C-rich fragments suggests that they may have been abrasion products from the surfaces of living or dead organisms. The proportions of biological particles and C-rich fragments

were highest in the coarse size fraction (in the $PM_{1\text{-}3.3}$ and especially in the $PM_{3.3\text{-}11}$ samples), which is in line with other individual particle studies related to continental background aerosol composition in Northern Europe (Ebert et al., 2000, 2004). No clear differences were observed in the proportions of biological particles and C-rich fragments related to the source regions of the air masses. They may have originated mainly from local forests, but transport from more distant regions is also possible.

In conclusion, the changes in aerosol source areas and meteorological conditions caused wide variation in the abundance of different particle types, and thus the concentrations and compositions of LRT particles can be very different even during successive days. Both accumulation mode particles ($PM_{0.2\text{-}1}$) and small-sized ($PM_{1\text{-}3.3}$) coarse mode particles may originate mostly from LRT in unpolluted rural regions. However, the composition of particles was totally different in these size fractions because they originated from distinct sources and/or through different formation pathways. During the pollution episode, the number proportions of anthropogenic particles (e.g. tar balls, metal oxides/hydroxides, spherical silicate fly ash particles and Ca-rich particles) increased clearly. As discussed elsewhere (e.g. Forsberg et al., 2005; Pope and Dockery, 2006), it would be very important to determine what kinds of particles are most detrimental to health.

4.3.2 Mixing state of particles and impacts on atmosphere

This section summarizes shortly some observations related to the mixing state of chemical components in different particle types of the $PM_{0.1\text{-}1}$ and $PM_{1\text{-}3.3}$ samples (**III**). Discussion of the hygroscopic and optical properties of particles is also presented.

$PM_{0.2\text{-}1}$ samples. The major particle groups in the $PM_{0.2\text{-}1}$ samples were 1) *soot* (0-12%) and 2) *(ammonium)sulphates and their mixtures with C, K, soot inclusions and/or other inclusions* (83-97%). The particles of the latter group were divided roughly into three subgroups to illustrate the strong internal mixing of particles; 2a) *(ammonium)sulphates mixed with recognizable soot* (2-22%), 2b) *(ammonium)sulphates mixed with vacuum-resistant and detectable C* (13-36%) and 2c) *(ammonium)sulphates without detectable C* (26-81%). Thus, internal mixing of C and S was a common occurrence in particles of the $PM_{0.2\text{-}1}$ size fraction. The presence of internally mixed (ammonium)sulphate particles with soot and/or other carbonaceous components is in line with other recent studies conducted in various continental environments (Hasegawa and Ohta, 2002; Lee et al., 2002; Pósfai et al., 2003; Dall'Osto et al., 2004; Okada et al., 2005; Tervahattu et al., 2005; Zhang et al., 2005).

Approximately 60% (range 25-100%) of soot particles were internally mixed with (ammonium)sulphates. Since some particles in the (ammonium)sulphates 'mixed with C' and 'without detectable C' subgroups may also have contained unidentifiable aged soot particles, the proportions for internally mixed soot/SO_4^{2-} particles should be considered as minimum estimates. While freshly emitted soot is extremely hydrophobic, aging processes such as coagulation, condensation and chemical reactions cause soot to become rapidly (under polluted conditions less than a few hours, Johnson et al., 2005) more hydrophilic (Zuberi et al., 2005). The internal mixing of soot with SO_4^{2-} (as well as with hygroscopic OC and NO_3^-) strengthens the light absorption properties of soot, thus increasing direct radiative forcing (Chung and Seinfeld, 2005; Schnaiter et al., 2005). However, the total effect of soot on the radiation balance of the earth is still difficult to estimate accurately, because the aging of soot decreases its poorly known surface area (see studies of van Poppel et al., 2005 and Adachi et al., 2007 based on

three-dimensional TEM images), shortens its residence time in the atmosphere due to more efficient wet deposition and enables soot to act as CCNs (Liu et al., 2005; Zuberi et al., 2005).

The proportions of (ammonium)sulphates mixed with vacuum-resistant and detectable C were also quite high (13-36%). Their proportions were higher during the pollution episode and the intermediate period (33-36%) than in the clean, marine period (13-17%). However, it is still insufficiently known what types of mixtures of (ammonium)sulphates, carbonaceous components and nitrate form in the atmosphere, how commonly these mixed particles occur and how strongly the changes in the mixing state affect the properties of these particles (e.g. impact on hygroscopic growth and reactions with gases) (Anttila and Kerminen, 2002; Kanakidou et al., 2005; Donaldson and Vaida, 2006; Sun and Ariya, 2006).

Tar balls were present in both the $PM_{0.2\text{-}1}$ and $PM_{0.1\text{-}3.3}$ size fractions during the pollution episode. They were mixed only slightly with SO_4^{2-} based on elemental and morphological observations (**III**). This result is consistent with other studies (Pósfai et al., 2003, 2004; Hand et al., 2005). Tar balls may scatter and absorb light strongly, and they do not exhibit deliquescence but do uptake some water at high levels of RH (~ higher than 60-80%, Hand et al., 2005; Semeniuk et al., 2007). Thus, they may play an important role in regional haze and climate forcing when the amount of aerosols from biomass burning is high.

$PM_{1\text{-}3.3}$ samples. This size fraction contained coarse particles showing the slowest rates of removal from the atmosphere, which makes them especially important from the climatic point of view. The major particle types in this fraction were 1) *silicates*, 2) *Ca/Mg carbonates, sulphates and/or nitrates* and 3) *sea salt*. Most silicates contained S, which probably accumulated on their surfaces through chemical reactions, condensation, coagulation and/or cloud processes during transport. This observation is in line with other studies of aged dust particles (e.g. Kojima et al., 2006; Sullivan et al., 2007). The SO_4^{2-} accumulation on the surface of the silicates can modify their CCN ability, thus changing the cloud formation properties and residence time of silicates. Mixing of mineral particles with secondary species can also alter the direct radiative properties of the dust (Bauer and Koch, 2005).

Ca-rich particles contained various mixtures of Ca and Ca/Mg carbonates, nitrates and sulphates. The substitution of CO_3^{2-} by SO_4^{2-} and NO_3^- is typical of Ca/Mg carbonates in the atmosphere, due to reactions with SO_2 and HNO_3 (Song and Carmichael, 1999; Al-Hosney and Grassian, 2005; Laskin et al., 2005b). These conversion products are highly hygroscopic (e.g. DRH for amorphous calcium nitrate $Ca(NO_3)_2$ particles is only ~13%, Tang and Fung, 1997). However, $Ca(NO_3)_2$ is highly soluble and readily deliquesces, while calcium sulphate ($CaSO_4$) is very hygroscopic but rather insoluble. In the $PM_{1\text{-}3.3}$ samples, several rounded Ca-rich particles appeared to be very thin (light contrast in TEM images), indicating that they were in liquid form during impaction on the TEM grids. During their sampling, the RH was only 30-31%, which shows that mixed Ca/Mg carbonates/sulphates/nitrates may also occur at least partly in liquid form, even at very low RH. This is consistent with the results of recent laboratory studies with environmental SEM (with adjustable RH) for Ca-rich particles collected from various environments (Laskin et al., 2005a, b). The substitution of CO_2^{3-} with SO_4^{2-} and NO_3^- from Ca/Mg-rich particles may alter their optical and CCN properties as well as residence time in the atmosphere (Gibson et al., 2006a, b). These reactions also provide a sink for SO_2 and HNO_3 and release CO_2. Ca-rich particles (and silicates) are removed

rapidly from the atmosphere due to their large sizes, which reduces the amounts of scavenged species in the atmosphere.

The rate of Cl^- depletion (calculated from Na/Cl ratio) in SSPs varied strongly between samples. Only a minor fraction of Cl^- was replaced with SO_4^{2-} or MSA in all $PM_{1\text{-}3.3}$ samples, since the S/Na was almost constant for most of the SSPs (**III**). This suggests that Cl^- was replaced mainly by NO_3^- , which is usually the most important Cl^--substituting anion together with SO_4^{2-} (Kerminen et al., 1997, 1998). Cl^- substitution by NO_3^- strongly alters the hygroscopic properties of SSPs; $NaNO_3$ may contain liquid water at much lower levels of RH than unreacted SSPs (Hoffman et al., 2004). Thus, modification of SSPs may alter their size, light-scattering properties and affinity for CCN formation. The presence of water on sea-salt surfaces also greatly enhances their reactivity with gases compared with dry sea salt (ten Brink, 1998; Hara et al., 2002). Furthermore, the NO_3^- and nss-SO_4^{2-} that accumulate in SSPs are removed rapidly from the atmosphere due to the large sizes of the particles, which reduces the amounts of scavenged species in the atmosphere.

In conclusion, significant internal mixing of chemical components both in the $PM_{0.2\text{-}1}$ and $PM_{1\text{-}3.3}$ size fraction was observed; (1) (ammonium)sulphates were often mixed with soot and other carbonaceous materials, (2) silicates, Ca/Mg-rich particles and SSPs were mixed with SO_4^{2-} and/or NO_3^-. This result is in line with other studies conducted for aged aerosols (section 2.2.7), which indicates that several chemical components of LRT aerosols are often present as internal mixtures. Thus, it would be better to treat these aged aerosol components as internal mixtures in global physicochemical and climate models.

4.4 Coarse particles over the Atlantic Ocean between Europe and Antarctica

The chemical composition of individual coarse (D_p ~1-3 μm) particles was studied with the SEM/EDX method from samples collected over the Atlantic Ocean between Europe and Antarctica during a voyage in November-December 1999 (**IV**). The main aim was to investigate the impacts of emissions from different continental sources on individual particle composition over the ocean. The distance from the coast (~ 100-2000 km) and the arrival route of air masses varied strongly during 23 sampling periods (Figs. 4a and b in section 3.3). Since the meteorological conditions and emissions showed interannual, seasonal and daily variation (Goudie and Middleton, 2001; Duncan and Bey, 2004; Carmona-Moreno et al., 2005; Quinn and Bates, 2005; Engelstaedter et al., 2006; van der Werf et al., 2006), the results represent the situation during the cruise. However, several interesting differences between the sampling regions were observed, which in general were quite consistent with the results of previous studies.

4.4.1 Individual particle types

The individual particles analysed were classified into seven particle types based on their elemental composition. Table 6 shows the particle types, classification criteria and mean elemental weight ratios of the particle types. The particle types were 1) sea salt, 2) Mg-sulphate, 3 Ca-sulphate, 4) mixed aluminosilicates and sea salt, 5) aluminosilicates, 6) Ca-rich particles and 7) Fe-rich particles. Finally, we formed the group ‘others’ for the remaining particles that did not belong to any of the particle groups mentioned above. This group contained mainly different sulphates (abundant S and some Na, Mg, Ca and/or K) and also some chlorides (abundant Cl and some Na, Mg, Ca and/or K). Table 7 shows the relative percentages of different particle types in each sample during the voyage. In most samples, the sea-salt group was clearly predominant compared with the

other particle types. However, the fractions of continental particles, such as aluminosilicates and Fe-rich particles, predominated near the coast of Africa (samples 7-11).

Table 6. Classification criteria and mean elemental weight ratios of particle types. Elemental weight ratios are semiquantitative and normalized to 100% (**IV**).

Particle type	Elemental classification criteria	Mean elemental weight ratios of particle types									n*
		Na	Mg	Al	S	Cl	K	Ca	Ti	Fe	
Sea salt	(Na+Cl)>30 and (Mg+K+Ca)<25 and Al<3	36	5	<1	7	48	1	1	<1	<1	1064
Mg-sulphate	Mg>20 and S>25	4	30	<1	58	<1	5	<1	<1	<1	59
Ca-sulphate	Ca>25 and S>20	5	1	2	39	2	2	47	<1	2	83
Mixed aluminosilicates and sea salt	Al>3 and [(Na>20 and Na/Al>1) or Cl>10]	22	10	21	11	15	7	4	1	11	147
Aluminosilicates	(Al>15 and Na/Al<1 and Cl<10 and Fe<60) or Ti>15	9	8	38	7	3	11	3	2	19	295
Ca-rich	Ca>60	2	1	<1	7	1	2	86	<1	<1	3
Fe-rich	Fe>60	7	4	5	2	2	1	<1	1	77	13
Other	-	17	17	3	29	10	7	13	1	3	36

* Number of analysed particles.

Table 7. Relative fractions (%) of different particle types during the voyage (**IV**).

Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
n*	100	100	100	100	100	100	100	100	100	100	50	50	50	50	50	50	50	100	50	50	50	50	50
Sea salt	71	57	60	90	62	59	5	2	2	28	40	78	84	96	94	98	96	92	94	96	98	98	100
Mg-sulphate	1	25	18	1	2	3	0	0	8	0	0	0	0	0	2	0	0	0	0	0	0	0	0
Ca-sulphate	7	3	1	6	7	5	14	16	5	5	6	2	6	0	0	2	2	0	6	4	0	0	0
Mixed aluminosilic. and sea salt	5	5	9	2	3	14	19	22	24	24	16	10	2	2	2	0	2	3	0	0	0	0	0
Aluminosilicates	6	5	8	0	20	18	57	58	55	39	32	10	6	0	2	0	0	4	0	0	0	0	0
Ca-rich	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe-rich	3	1	0	1	0	0	1	1	3	0	4	0	0	0	0	0	0	1	0	0	0	0	0
Other	7	4	4	0	6	1	1	1	3	4	2	0	2	2	0	0	0	0	0	0	2	2	0

* Number of analysed particles.

4.4.2 Chloride depletion from sea-salt particles

The substitution of Cl^- by acid anions in individual SSPs was studied by observing the elemental weight ratios of Na, Cl and S in the samples (**IV**). Anions of strong acids, such as NO_3^- and SO_4^{2-} are usually the most important Cl^--substituting compounds (Kerminen et al., 1998; Mouri et al., 1999; Ro et al., 2001; Li et al., 2003a). They also explained practically all of the Cl^- depletion also during this voyage based on the bulk chemical results of Virkkula et al. (2006b) and the present SEM/EDX results.

There were major differences in the modification of SSPs by acidic compounds in the samples studied (**IV**). Cl^- depletion was strongest when air masses arrived from the direction of the anthropogenic pollution sources. The relative amounts of moderately (~20-90% of Cl^- lost from individual SSPs) and strongly (>90% of Cl^- lost) modified SSPs were very high in the North Atlantic Ocean and especially near Europe (65-74% of SSPs). The Cl^- depletion was mainly caused by SO_2 and NO_x emissions from continental sources and possibly also from the ship.

The amount of modified SSPs was also high (56-87%) near the Canary Islands, similar to that of samples collected near continental Europe. Anthropogenic emissions from the Canary Islands and ship traffic emissions (Song et al., 2003) may be the main reason for Cl^- depletion, since the ship was sailing on a busy sea lane between Europe, Africa and

South America (Capaldo et al., 1999; Lawrence and Crutzen, 1999). Emissions from continental Africa may also increase Cl^- depletion.

Near the Gulf of Guinea, the fraction of moderately and strongly modified SSPs was 34%, and the acidic compounds probably originated partially from biomass burning. The continental impact decreased strongly farther from the coast of Western Africa, where only 10-20% of the SSPs were modified by acidic gases. The proportion of reacted SSPs was lowest (~1%) between Africa and Antarctica, when the ship was far from the coasts and air masses arrived from the direction of the clean sea areas. When the ship was sailing in the pack ice area off the Antarctic coast, the SSPs originated farther from the open sea and some (14%) were modified moderately by acidic compounds during transport.

In conclusion, individual particle results obtained with SEM/EDX were consistent with the bulk chemical results. Furthermore, the SEM/EDX results showed wide internal variation within samples, which could not be observed with the bulk chemical methods. In the same sample, the rate of Cl^- depletion of single particles often varied strongly and Cl^- was substituted by SO_4^{2-} or NO_3^- or both (**IV**). This observation is in line with other individual particle studies (e.g. Pósfai et al., 1995; Mouri et al., 1999; Ro et al., 2000 ; Ro et al., 2001; Hara et al., 2002, 2005; Li et al., 2003a; Hwang and Ro, 2006b).

The LRT particles and their precursor gases from continental sources strongly impact the chemical composition of sea salt in coastal areas, as was observed here and in numerous other field studies (e.g. Quinn and Bates, 2005). The abundant Cl^- of SSPs was substituted by SO_4^{2-} and NO_3^-. Sea salt is an important sink for gaseous species producing nss-SO_4^{2-} and NO_3^- as well as a source for atmospheric Cl, thus implying major effects on the atmosphere. Nss-SO_4^{2-} and NO_3^- accumulated in SSPs are removed rapidly from the atmosphere, due to the large sizes of the SSPs, which reduces the amounts of scavenged species in the atmosphere. For example, the model simulations of Gong and Barrie (2003) indicated that the presence of sea salt increases the mass median diameter of SO_4^{2-} aerosols by up to a factor of 2 over the marine boundary layer (MBL) with high sea-salt concentrations and reduces the global SO_4^{2-} aerosol mass in the surface MBL from 5 to 75%, depending on the sea salt distributions. This change reduces the fraction of nss-SO_4^2 aerosol as CCNs, which may decrease the cloud droplet number concentrations over oceans, thus changing the lifetimes and optical properties of clouds (Gong and Barrie, 2003). The modification of SSPs also changes their own chemical properties, such as deliquescence and re-crystallization points, as was already discussed in section 4.3.2.

4.4.3 Mg-sulphate particles and other fractional recrystallization products

In some SSPs, the Mg, K or Ca fractions differed clearly from the ratios of these elements to Na in seawater. The elemental ratios indicated that there were different mixed Mg, K or Ca sulphates and chlorides, a few $CaCl_2$ and $MgCl_2$ and many sulphate particles, that contained mainly Mg or Ca and only minor amounts of Na. The particles were classified into the Mg-sulphate and Ca-sulphate groups or were left in the unclassified (‘others’) particle group (Tables 6 and 7). These types of marine particles are formed mainly by fractional recrystallization of SSPs (Borchert, 1965; Parungo et al., 1986). However, some of these different cation sulphate particles may also have originated from continental sources or formed through the coagulation of SSPs and continental particles containing the same elements as in seawater. Ca-sulphate particles in particular have both marine and continental sources. The marine formation

mechanisms of Ca-sulphate particles include fractional recrystallization of SSPs and reactions of marine $CaCO_3$ with SO_2 in the atmosphere. Marine $CaCO_3$ may originate from fractional recrystallization of SSPs or from marine organisms such as coccoliths (Andreae et al., 1986). The Ca-sulphate particles probably originated from marine sources in remote sea areas (e.g. samples 19 and 20), but the highest amounts of Ca-sulphate particles near the coasts indicated that part of the Ca-sulphates originated from continental sources.

Various crystallization products (chlorides, sulphates, nitrates and carbonates of Na^+, Mg^{2+}, K^+ or Ca^{2+} and different mixtures of these chemical components) of SSPs were observed in many studies (Parungo et al., 1986; Anderson et al., 1992; Artaxo et al., 1992; Pósfai et al., 1994; Anderson et al., 1996; Ro et al., 2001; Li et al., 2003a). However, the fraction of Mg-sulphate particles was 18-25% in two samples (samples 2 and 3) near Europe, which is a higher percentage than in any study we have seen. In addition to Mg and S, particles in the Mg-sulphate class often contained minor amounts of K and/or Na (**IV**). The mean size of the Mg-sulphate particles was 3.4 μm, which is clearly higher than the mean sizes of other particle types (1.7-2.1 μm). Since the continental source or ship traffic source of Mg-sulphate particles seemed very unlikely (**IV**), we assume that the Mg-sulphate particles were formed mainly from S-rich SSPs as crystallization and fractionation products.

When water evaporates from seawater droplets, different compounds crystallize separately according to their solubility products (Borchert, 1965; Eugster et al., 1980; Zayani et al., 1999). After evaporation SSPs may form aggregates of loosely attached crystals that can shatter and produce pure crystals and crystal mixtures. However, several studies addressed the question of whether crystallization and shattering occur before or after sampling (Parungo et al., 1986; Mouri et al., 1997; De Bock et al., 2000; Ro et al., 2001). In our samples, some Mg-sulphate particles were clearly larger than the SSPs, which suggests that they may have formed during or after sampling (**IV**). However, the formation pathway of these particles remained uncertain.

In conclusion, various fractional recrystallization products of sea salt were observed here. These types of particles have been reported previously, but it is still poorly known how common these fractionally crystallized and shattered particle types are in the atmosphere, and how they affect the atmospheric processes related to chemistry of SSPs. As mentioned above, the hygroscopicity of SSPs varies, depending on their composition, which affects both their reactivity with gases and sizes at different levels of RH.

4.4.4 LRT of continental particle types and their sources

The relative proportions of particles from (total natural and/or anthropogenic) continental sources were calculated, using the following source estimates for different particle types (**IV**). Aluminosilicates and Fe-rich particles were assumed to originate totally from continental sources. The origin of Ca-rich particles (present only in one sample near the coast of Africa) was also very likely continental only, since they contained some P and the amounts of marine elements such as Na and Cl were negligible. The Ca-sulphate particles originated from both continental and marine sources as discussed above. Since the fractions of these sources were impossible to distinguish, we used equal fractions as a coarse estimate. This ratio probably underestimated the fraction of continental sources when air masses arrived from the direction of the continents and overestimated continental sources in remote marine

areas. 'Mixed aluminosilicates and sea-salt' class was also divided equally between continental and marine sources. All other particle groups (SSPs, Mg-sulphate particles and particles in the group 'other') were considered marine particles, although some of these particles also contained compounds (e.g. nss-SO_4^{2-} and NO_3^-) that had accumulated mainly from continental emissions and/or from ship traffic emissions in some samples.

The relative number proportion of continental particles was 10-15% near Southern Europe, 5-28% near Northwestern Africa and 47-78% between the coast of Mauritania and Liberia (**IV**). The bulk chemical results of nss-Ca^{2+} of Virkkula et al. (2006a) also confirmed the high amount of continental particles near the coast of Africa (**IV**). In the remote sea areas west and south of the South Africa, the fraction of continental particles was only 1-3% and near Cape Town 7%. There were no continental particles in the remote sea areas near Antarctica.

Aluminosilicates and aluminosilicates mixed with sea salt were clearly the most common continental particle types in the samples collected near the coasts of Europe and Africa (Table 7). Some Ca-sulphate and a few Fe-rich particles were also observed. The majority of aluminosilicates and Fe-rich particles were clearly soil dust, but near industrial areas some of these particles may have been fly ash from different industrial processes and fossil fuel burning. Ca-sulphate particles also originate from various continental sources including fossil fuel burning, cement and metal industries, soil dust and biomass burning (Hoornaert et al., 1996; Li et al., 2003b). Some of the continental Ca-sulphate particles are formed from $CaCO_3$ that had reacted with SO_2 in the atmosphere. The continental $CaCO_3$ originates from the cement and metal industries and from soil dust (Hoornaert et al., 1996).

The relative proportions of continental particles were very high in the samples collected near Northern Africa. The NAAPS model results indicated that there was significant Saharan dust outflow from the direction of the Western Sahara and Mauritania (**IV**). The chemical composition of aluminosilicates in these samples analysed with SEM/EDX indicate windblown Saharan dust as the main source (Husar et al., 1997; Goudie and Middleton, 2001; Prospero et al., 2002). The relatively high amounts of Ca-sulphate particles (Table 7) and very high nss-Ca^{2+} (**IV**, Virkkula et al., 2006a) are evidence of Ca-rich minerals, such as $CaCO_3$ and gypsum ($CaSO_4 \cdot 2H_2O$), that are common in northern and western Sahara (Chiapello et al., 1997; Claquin et al., 1999; Goudie and Middleton, 2001).

The NAAPS model results indicated that outflow of dust particles decreased gradually when the ship was sailing from coastal areas of Senegal towards the Gulf of Guinea. At the same time, the NAAPS model indicated a large smoke plume originating from biomass burning (**IV**). The bulk chemical results of Virkkula et al. (2006a) also showed that these samples contained abundant nss-K^+ which indicated biomass burning as the major source of these aerosols (**IV**). The savanna zone located between Senegal and Sudan is one of the strongest and largest biomass-burning emission sources in the world (Liousse et al., 1996; Husar et al., 1997; van der Werf et al., 2006; Koch et al., 2007). The SEM/EDX results indicated that aluminosilicates were mixed with sea salt and continental gaseous compounds during their transport to the oceanic sampling sites.

In conclusion, various continental particle types were observed near the coasts of Europe and Africa. The transport of continental particles over oceans has significant climatic effects and they also transport materials in seawater. The transport of mineral dust from Northern Africa to the ocean was strong during the voyage, and Chiapello et

al. (1999) observed that African dust controls the total aerosol optical depth over these sea areas (at Sal Island, Cape Verde), even in the absence of dust outbreaks during winter. Most of the aluminosilicates studied contained at least some S (see Table 6) and $CaCO_3$ particles were almost totally absent. The S content of aluminosilicates in soil is very low, and Saharan dust also contains $CaCO_3$ (Claquin et al., 1999). Thus it seems likely there has been accumulation of SO_4^{2-} on the surfaces of aluminosilicates and substitution of CO_3^{2-} by SO_4^{2-} and/or NO_3^- from $CaCO_3$ particles. This emphasizes the importance of surface reactions on continental particles, which alters their own optical and hygroscopic properties as well as affects the concentrations of other climatologically important chemical components of the atmosphere, as was discussed in section 4.3.2.

In addition to atmospheric impacts, continental particles also alter the composition of seawater when they are deposited in the ocean. Large amounts of continental particles are deposited in coastal, biologically active waters. Nutrients derived from continental aerosols are important factors affecting primary productivity in oceans; e.g. atmospheric deposition of desert dust is a significant source of Fe in oceans (Martin et al., 1994; Sarthou et al., 2003; Jickells et al., 2005; Mahowald et al., 2005).

5. SUMMARY AND CONCLUSIONS

Frequency of LRT episodes of fine particles in southern Finland

A long-term survey of LRT episodes of fine particles in the Helsinki metropolitan areas was compiled for the years 1999-2006. The following criteria were defined for the detection of $PM_{2.5}$ LRT episodes in the Helsinki metropolitan area: the 24-h moving average $PM_{2.5}$ concentration is higher than 25 μg m^{-3} at the Kallio urban background site, and the particle concentrations increase simultaneously to high levels at the Luukki regional background site. During the LRT episodes, the 24-h $PM_{2.5}$ concentration varied between 25 and 49 μg m^{-3}, which is 3-6 times higher than the mean value (8.6 μg m^{-3}) during 1999-2006. The number of LRT episodes varied between 1 and 7 per year during 1999-2006, the total number being 37. On a monthly level, the LRT episodes occurred most often in February (# 6), March (# 6), April (# 9), August (# 4) and September (# 4). The duration of individual episodes varied between 0.1 and 8.7 d. The total duration of all episodes per year was 0.6-15.0 d. Only hours with 24-h $PM_{2.5}$ moving average > 25 μg m^{-3} were included in the duration, and thus weaker episode stages were not counted. The following conclusions could be made;

- LRT causes high $PM_{2.5}$ peaks every year in southern Finland but there is strong interannual variation in the number, strength and duration of episodes.
- LRT episodes occur most frequently during late winter, spring and late summer.
- The annual mean $PM_{2.5}$ concentrations are low in Finland but during the LRT episodes the daily values exceed the updated WHO guideline value (25 μg m^{-3}) for the 24-h $PM_{2.5}$ mean concentrations.

Particle sources and sizes during LRT episodes in southern Finland

Four LRT pollution episodes that occurred in southern Finland in 2002 (17-22 March, 12-15 August, 26-28 August, 5-6 September) were selected for in-depth investigations. (Furthermore, one (fifth) LRT episode was investigated in detail using different methodological combinations, and that study is summarized in the next paragraph.) Backward air mass trajectories, satellite detections of fire areas and dispersion-modelling results indicated that emissions from open biomass-burning fires in Eastern Europe arrived over Finland during these episodes. Daily particle samples from long-term mass monitoring measurement were analysed using the SEM/EDX method. The proportions of S-rich particles and agglomerates (agglomeration was caused partly by the sampling method used) increased during the episodes and they contained elevated fractions of K, indicating emissions from biomass burning. These aerosols were mixed with S-rich emissions from fossil fuel burning during transport, since the air masses came through polluted areas of Europe. Minor amounts of coarse Ca-rich particles were also brought in by LRT during the August and September episodes, probably originating from wildfires and/or from Estonian and Russian oil-shale-burning industrial areas. Most of the particle mass was in the $PM_{2.5}$ size fraction during all episodes. Particle number size distribution measurements with DMPS revealed that concentrations of accumulation mode particles (90-500 nm) increased during the episodes, while concentrations of particles in the Aitken (25-90 nm) and nucleation (3-25 nm) modes decreased. The reduction in number of the smallest particles was caused by uptake of vapours and molecular clusters by LRT particles. The following conclusions could be made;

- Based on this thesis and other studies, the strongest and longest LRT pollution episodes of fine particles in southern Finland are caused by emissions from open biomass burning, but emissions from ordinary anthropogenic sources (e.g. from energy production, traffic, industry and residential burning) in Eastern Europe also cause significant LRT episodes (see also next paragraph).
- The smoke from open biomass burning is an important factor in the deterioration of air quality locally and occasionally even regionally in the eastern parts of Europe,

especially during warm and dry periods in spring and late summer. Emissions from agricultural waste burning in fields and wildfires in Eastern Europe can deteriorate air quality over very large areas, even at distances of over 1000 km from the fire areas.

- Particle mass concentration in the $PM_{2.5}$ size fraction and number concentration in the accumulation mode size range increase strongly during LRT pollution episodes, while the number concentrations of smaller particles remain low or decrease due to LRT.
- The daily fine particle samples from routine mass-monitoring measurements are not ideal for detailed individual particle analysis with the SEM/EDX method, due to agglomeration of particles during sampling and sample preparation. Despite this, they can be utilized successfully to identify major changes in elemental composition and emission sources of particles during different episodes.

Composition and origin of *individual* particles during polluted and unpolluted LRT periods in southern Finland

The chemical composition, morphology, mixing state and sources of individual aerosol particles at a background site (Hyytiälä) in southern Finland were studied during an LRT pollution episode (PM_1 ~16 μg m^{-3}, backward air mass trajectories from the southeast), an intermediate period (PM_1 ~5 μg m^{-3}, backtrajectories from the northeast) and clean periods (PM_1 ~2 μg m^{-3}, backtrajectories from the northwest/north) in May 2004. Particles in three size fractions ($PM_{0.2\text{-}1}$, $PM_{1\text{-}3.3}$ and $PM_{3.3\text{-}11}$) were analysed, using the TEM/EDX method. The major particle types in the $PM_{0.2\text{-}1}$ samples were 1) soot and 2) (ammonium)sulphates and their mixtures with variable amounts of C, K, soot and other inclusions. The number proportions of these two particle groups in the $PM_{0.2\text{-}1}$ samples were 0-12% and 83-97%, respectively. During the pollution episode, the proportion of Ca/Mg-rich particles was very high (26-48%) in the $PM_{1\text{-}3.3}$ and $PM_{3.3\text{-}11}$ samples, while the $PM_{0.2\text{-}1}$ and $PM_{1\text{-}3.3}$ samples contained elevated proportions of silicates (4-33%, including also spherical fly ash particles), metal oxides/hydroxides (1-9%) and tar balls (1-4%). These aerosols originated mainly from polluted areas of Eastern Europe, and some open-biomass burning smoke was also brought in by LRT. During the intermediate period, the $PM_{1\text{-}3.3}$ samples contained large numbers of porous (spongelike) Na-rich particles with abundant S, K and O, which could have originated from the burning of wood pulp wastes in the paper industry. When air masses arrived from the Arctic Ocean during the clean period, the $PM_{1\text{-}3.3}$ samples contained abundant SSPs with variable rates of Cl^- substitution (mainly by NO_3^-). The proportions of biological particles and C-rich fragments (probably also of biological origin) were highest in the $PM_{3.3\text{-}11}$ samples. The following conclusions could be made;

- The proportions of several particle types (e.g. tar balls, metal oxides/hydroxides, spherical silicate fly ash particles and/or Ca/Mg-rich particles) from anthropogenic activities in Eastern Europe increase during LRT pollution episodes in southern Finland compared with unpolluted periods in northern marine source areas regarding aerosols.
- Changes in aerosol source areas and meteorological conditions cause wide variation in the abundance of different particle types, and thus the concentrations and compositions of LRT particles can be very different even during successive days.
- Both accumulation mode particles ($PM_{0.2\text{-}1}$) and small-sized coarse particles ($PM_{1\text{-}3.3}$) may originate mostly from LRT in unpolluted rural regions, but the composition of these fractions may be totally different. In the $PM_{0.2\text{-}1}$ size range, the major particle group is '(ammonium)sulphates and their mixtures with variable amounts of C, K, soot and/or other inclusions', independent from air mass history. In the $PM_{1\text{-}3.3}$ size range, the major particle types are various Ca/Mg-rich particles, silicates, aged sea salt and/or '(ammonium)sulphate and their mixtures', depending strongly on air mass history.
- Strong internal mixing of chemical components in particles is typical for LRT aerosols; (1) (ammonium)sulphate is often mixed with soot and other carbonaceous

materials, (2) silicates, Ca/Mg-rich particles and SSPs are mixed with SO_4^{2-} and/or NO_3^-. Thus, the aging of particles has significant impacts on their chemical, hygroscopic and optical properties, which can largely alter the environmental and health effects of LRT aerosols. It would be better to treat these aged aerosol components as internal mixtures in global physicochemical and climate models.

- Neither bulk chemical nor individual particle analysis method alone is sufficient to understand and describe in detail the chemical composition of aerosols, which is an important factor related to their optical and hygroscopic properties that affect their direct and indirect radiative forcing and their reactivity with gaseous components.

Continental impact on composition of *individual* coarse particles over the Atlantic Ocean between Europe and Antarctica

The composition of small-sized (D_p ~1-3 μm) coarse particles was studied over the Atlantic Ocean between Europe and Antarctica during a voyage in November-December 1999. Individual aerosol particles were analysed using the SEM/EDX method. The major particle types observed were fresh sea salt, SSPs reacted partly or totally with H_2SO_4 or HNO_3, Mg-sulphate, Ca-sulphate, mixed aluminosilicates and sea salt, aluminosilicates, Ca-rich particles and Fe-rich particles. The relative fractions of SSPs with moderate or strong Cl^- depletion were high near the coasts of Europe (65-74%) and Northern Africa (44-87%), low far from the coast of Western Africa (10-20%) and very low in remote sea areas between Africa and Antarctica (~1%). The Cl^- depletion was strongest when air masses arrived from the direction of anthropogenic pollution sources. The fractions of Mg-sulphate particles were high (18-25%) in two samples near Europe. The Mg-sulphate particles were probably formed as a result of fractional recrystallization of SSPs in which Cl^- was substituted by SO_4^{2-}. It remained unclear whether these particles were formed in the atmosphere or during and after sampling. The relative fractions of particles from continental sources were quite low (10-15%) near Europe, very high (25-78%) near the coast of Northwestern Africa and very low in the remote sea areas (0-2%). Most of the continental particles were aluminosilicates and some were internally mixed with sea salt. Near the coast of Northwestern Africa the main source of aluminosilicates was Saharan dust, and near the Gulf of Guinea emissions from biomass burning were also mixed with aluminosilicates and sea salt. The following conclusions could be made;

- LRT of different continental aerosol plumes significantly alter the composition of small-sized coarse particles over the ocean far (at least from hundreds to thousand(s) of kilometres) from the coasts, depending on the distance of different emission sources and on meteorological conditions. Thus, the LRT of continental aerosols has significant impacts on the chemico-optical properties of the marine boundary-layer atmosphere and seawater composition.
- The amounts of continental aerosols from different sources are highly variable in time and space near various continental regions (e.g. pollutants from industrialized Europe, desert dust from the Sahara and biomass-burning aerosols near the Gulf of Guinea).
- The Cl^- depletion from SSPs is high near the coasts of Europe and Africa when air masses arrive from polluted continental regions. Sea salt is an important sink for gaseous species producing nss-SO_4^{2-} and NO_3^- as well as a source for atmospheric Cl, thus significantly affecting properties of the atmosphere.
- Individual particle analysis shows wide internal variation in sea-salt composition due to Cl^- substitution by SO_4^{2-} and/or NO_3^-, as well as to fractional recrystallization and shattering of SSPs. At least part of the fractional recrystallization may occur during or after sampling.
- Integration between different measurement techniques is needed to capture the wide variation in properties and sources of aerosols at different sites and times.

6. FURTHER RESEARCH CONSIDERATIONS

In this thesis, both the SEM/EDX and TEM/EDX methods were used and combined with the results of other methods to determine the properties and sources of LRT aerosol particles. Electron microscopy provided valuable information on the morphology, internal structure, elemental composition and mixing state of chemical components in aerosols, which could not be obtained with bulk chemical methods. It would be desirable in future investigations to use electron microscopes that could be used in the cryomode, which prevents the evaporation of semivolatile compounds and reduces damage caused by the electron beam (Worobiec et al., 2003). Furthermore, it would be fruitful to use EDX which would be more sensitive for N analysis (Ro et al., 2000; Laskin et al., 2006) or electron energy-loss spectroscopy (EELS) for light-element analysis (Pósfai et al., 2004). Electron microscopes with environmental cells (e.g. adjustable RH and pressure) are very useful tools for studies of hygroscopicity (Krueger et al., 2003; Laskin et al., 2006; Semeniuk et al., 2007). Three-dimensional imaging with tomography is also a useful method for describing particle shapes and morphology (Adachi et al., 2007).

Electron microscopy analysis is time-consuming work, and therefore only limited numbers of samples can be studied. Furthermore, information on molecular composition is indirect and limited. Therefore, the most valuable results can often be obtained during field campaigns or laboratory experiments when various properties of aerosols are measured simultaneously with different (on-line and off-line) analysis methods to obtain a comprehensive view.

In this thesis, the sources and properties of aerosols were studied during various periods and in various environments. Several open questions worth investigating in further studies were recognized, and some are mentioned below:

Emissions from open biomass burning in Eastern Europe

- The impact of open biomass-burning emissions on air quality in Eastern Europe and surrounding regions is poorly quantified, although quite strong pollution episodes are observed every year. Thus, it would be important to study the emissions and air quality impacts of open biomass burning in Eastern Europe and try to find ways to reduce and forecast them. In future, the emissions from ordinary anthropogenic sources (e.g. traffic, energy production, industry and residential burning) are projected to decrease in most regions of Europe, while the emissions from wildfires may increase due to warming climate (more often dry and hot periods), if fire prevention and suppression measures are not intensified.

Individual particle chemistry and mixing state

- Recent off-line and on-line studies have shown various internal mixtures of chemical components in individual particles. However, it is still poorly understood how different chemical components are located in single particles. For instance, the liquid phases of particles may be covered with thin surfactant films that may alter their chemical and hygroscopic properties. Therefore, it would be desirable to investigate the surface and internal chemistry of individual particles (gradients between the surface and inner core of particles) and to evaluate their potential climatic impacts.
- In marine environments, the presence of different sea-salt crystallization products (fractional recrystallization and shattering) is not well understood. It is also poorly known how often and what types of mixtures marine biogenic carbonaceous products form with SSPs. The changes in mixing state of marine aerosols may significantly impact the hygroscopic and optical properties of particles.

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